Density Functional Theory: Basic Ideas & Applications

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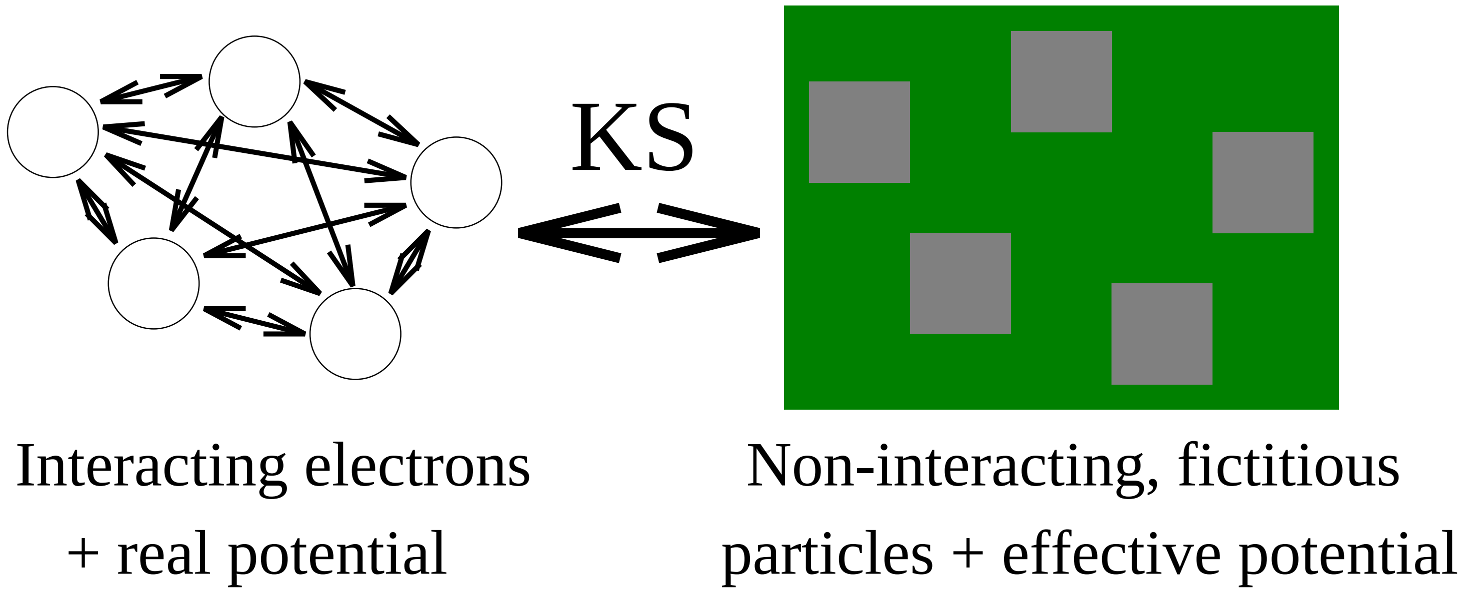
The Problem: Electron exchange & correlation in solids ($\approx 10^{23}$).

A Solution: Hohenberg-Kohn theorems and Kohn-Sham approach.



The Hamiltonian:

$$\hat{H} = \hat{T} + \hat{V}_{Hartree} + \hat{V}_{external} + \hat{V}_{xc}$$

V_{xc} = Hermitian, local, energy-independent exchange-correlation potential.

The Local Density Approximation

Some Extensions

Current Topics

An Alternative: Green Functions

Conclusion

The Hohenberg-Kohn Theorem

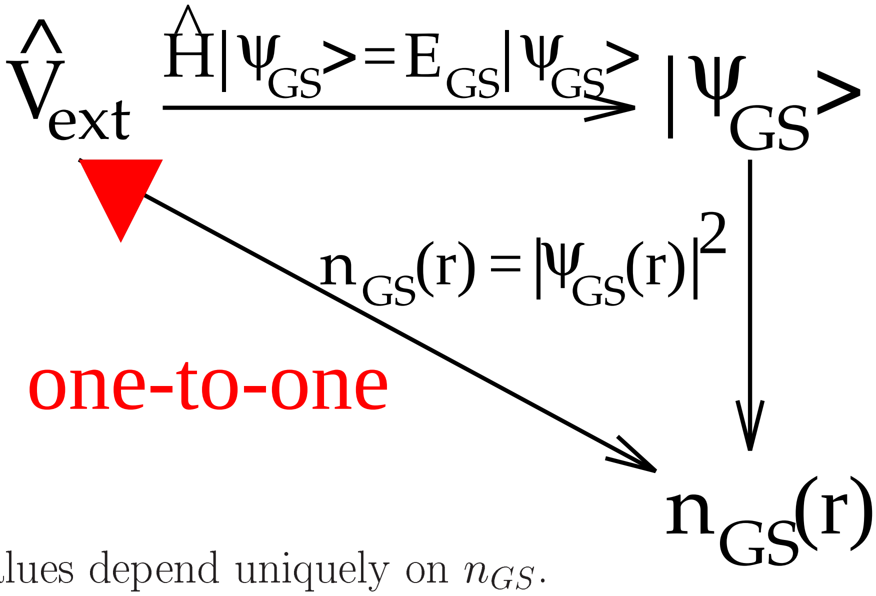
Many-electron Hamiltonian (ions fixed)

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i<j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^{N} V_{ext}(\mathbf{r}_i) = \hat{T} + \hat{V}_{C(oulomb)} + \hat{V}_{ext}.$$

$\hat{V}_{ext}$ = external, local, one-particle potential; E_{GS} = ground state energy;

$|\Psi_{GS}\rangle$ = non-degenerate ground state N-electron wave function.

HK theorem: Each local one-particle potential $\hat{V}_{ext}$ corresponds to exactly one ground state density $n_{GS}(\mathbf{r})$.



So what?

- Ground state expectation values depend uniquely on n_{GS}.

$$n_{GS} \Rightarrow \hat{V}_{ext} \Rightarrow \hat{H} \Rightarrow |\Psi[n_{GS}]\rangle \Rightarrow O[n_{GS}] = \langle\Psi[n_{GS}]|\hat{O}|\Psi[n_{GS}]\rangle$$

- $n_{GS}(x, y, z)$, not $\Psi_{GS}(x_1, y_1, z_1, ..., x_N, y_N, z_N)$, is the basic variable.

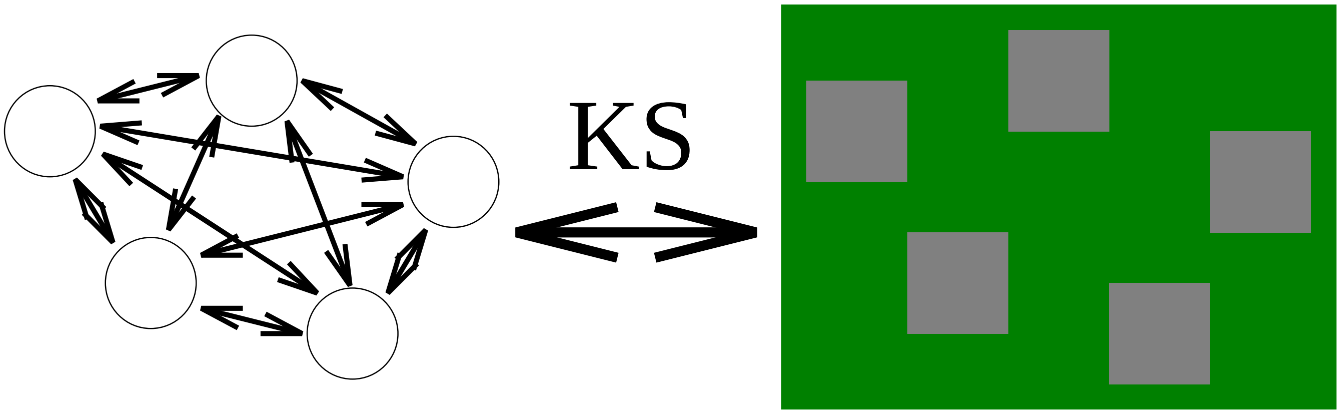
- Determine E_{GS} and n_{GS} via constrained minimization of the energy functional $E[n]$ (N = total number of particles, $|\Psi[n]\rangle$ = functional of density):

$$E[n] := \langle\Psi[n]|\hat{T} + \hat{V}_C + \hat{V}_{ext}|\Psi[n]\rangle \geq E_{GS}, \quad E[n_{GS}] = E_{GS},$$

$$\delta\left(E[n] - \mu\left(N - \int_V n(\mathbf{r})d\mathbf{r}\right)\right) = 0.$$

But still ... What about $\langle\Psi[n]|\hat{T}|\Psi[n]\rangle$ and $\langle\Psi[n]|\hat{V}_C|\Psi[n]\rangle$?

The Kohn-Sham Approach: Treating $\langle\Psi[n]|\hat{T}|\Psi[n]\rangle$ & $\langle\Psi[n]|\hat{V}_C|\Psi[n]\rangle$



Interacting electrons + real potential

Non-interacting, fictitious particles + effective potential

Take N fictitious, non-interacting particles moving in an effective potential.

$|\Phi_i\rangle$ = independent-particle wave function;

density: $n_{KS}(\mathbf{r}) = \sum_{i=1}^{N} |\Phi_i(\mathbf{r})|^2$; kinetic energy: $T_{KS} = -\frac{1}{2}\sum_{i=1}^{N}\langle\Phi_i|\nabla^2|\Phi_i\rangle$.

- **Kohn-Sham Assumption:** $n_{KS}(\mathbf{r}) = n(\mathbf{r})$.

- **Kohn-Sham Energy Partitioning**

$$E[n] = T_{KS}[n] + E_{H(artree)}[n] + E_{ext}[n] + E_{xc}[n]$$

$$E_{H(artree)}[n] = \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'; \quad E_{ext}[n] = \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$

$E_{xc}[n]$ = exchange and correlation beyond the Hartree approximation.

- **Kohn-Sham Equations** (variational minimization of $E[n]$)

$$\left[-\frac{1}{2}\nabla^2 + V_H(n_{GS};\mathbf{r}) + V_{ext}(n_{GS};\mathbf{r}) + V_{xc}(n_{GS};\mathbf{r})\right]\Phi_i(\mathbf{r}) = \varepsilon_i\Phi_i(\mathbf{r})$$

The Kohn-Sham Approach

- Local, Hermitian, energy-independent exchange-correlation potential contains all the complexities of the many-electron system:

$$V_{xc}(n_{GS};\mathbf{r}) = \left.\frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}\right|_{n=n_{GS}}$$

- Simple single-particle rather than N-electron equation to solve.
- Except for $\mu = \varepsilon_N$, ε_i are Lagrange parameters without physical meaning.
- Very efficient implementations on workstations & supercomputers.

What to do about V_{xc}?

⇒ The Local Density Approximation

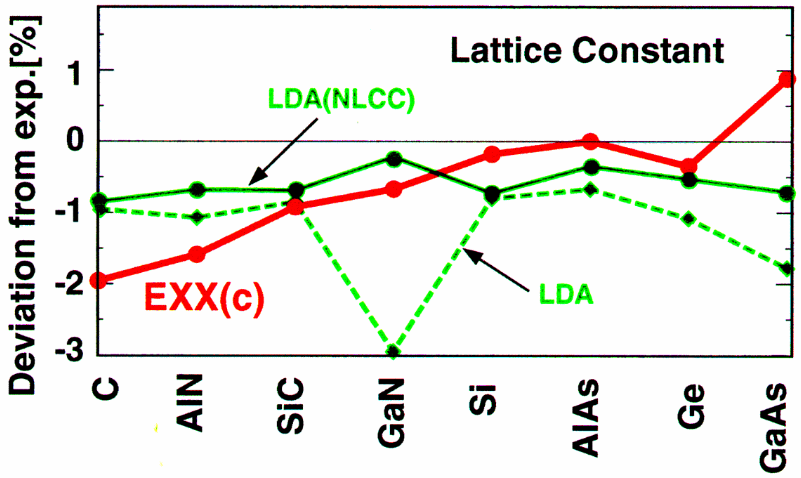
- We know the exchange-correlation (XC) potential of the **homogeneous electron gas** as a function of density.
- The approximation: Assume slowly varying density:

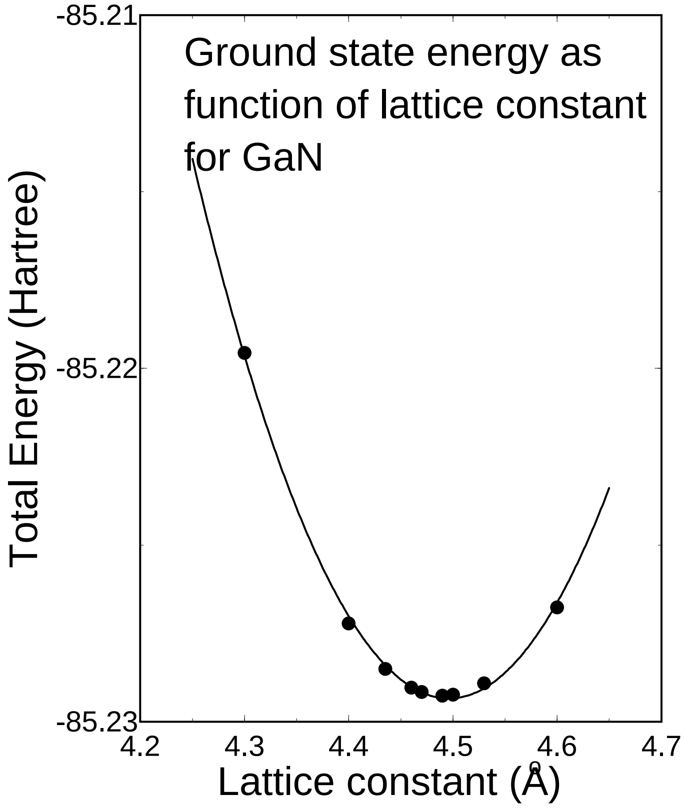
$$\left.\begin{array}{c}\text{inhomogeneous system at point } \mathbf{r} \\ \text{with } \textbf{local} \text{ density } n(\mathbf{r})\end{array}\right\} \approx \left\{\begin{array}{c}\text{homogeneous electron gas} \\ \text{with } \textbf{same} \text{ density } n(\mathbf{r})\end{array}\right.$$

$$E_{xc}^{inhom} \approx \int n(\mathbf{r})\varepsilon_{xc}^{hom}(n(\mathbf{r}))d\mathbf{r} \qquad V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

The Local Density Approximation works for structural properties.

- Lattice constants to within -1%.





LDA(NLCC) = approximate treatment of core electrons.

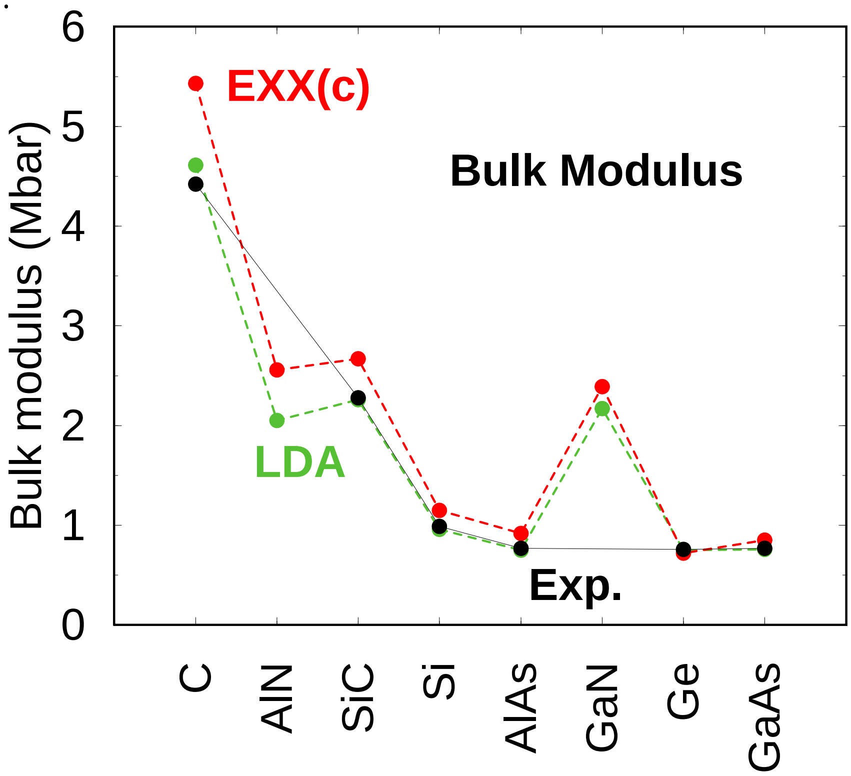
LDA = core electrons not treated.

- Bulk moduli B to within $\pm 10\%$.

$$B = -V \left.\frac{\partial P}{\partial V}\right|_{V_0} = -V \left.\frac{\partial^2 E}{\partial V^2}\right|_{V_0}$$

V = crystal volume,

$P = \partial E/\partial V$ = pressure.



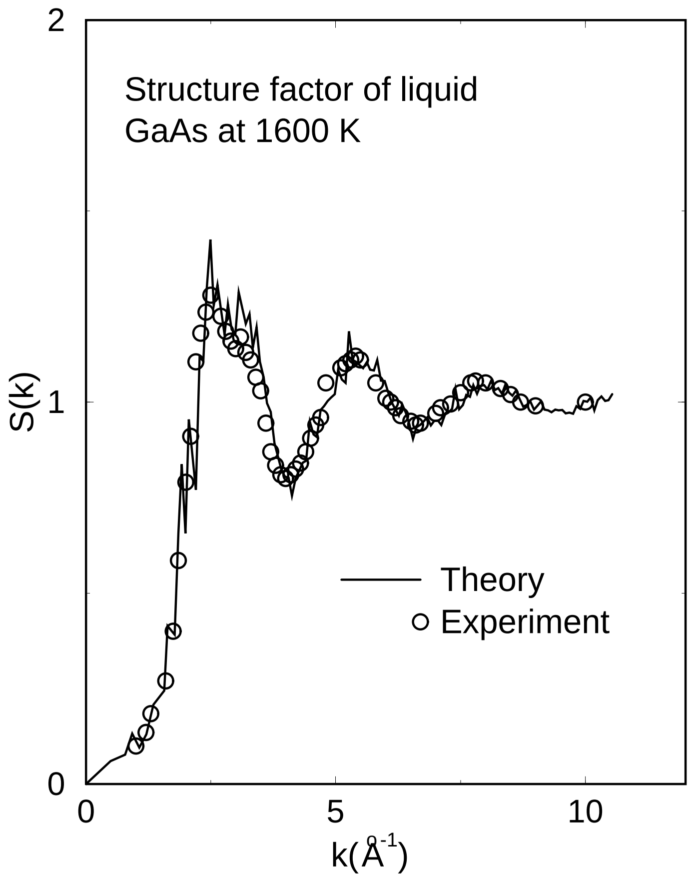
The Local Density Approximation works for structural properties.

- Structure factor ($\Rightarrow$ pair correlation function) to within a few percent:

$$S(\mathrm{k}) = \frac{1}{N}\langle \rho_{\mathbf{k}}\rho_{-\mathbf{k}}\rangle - N\delta_{\mathbf{k},0}$$
$$\rho(\mathbf{k}) = \sum_n e^{-i\mathbf{k}\cdot\mathbf{R}_n}$$

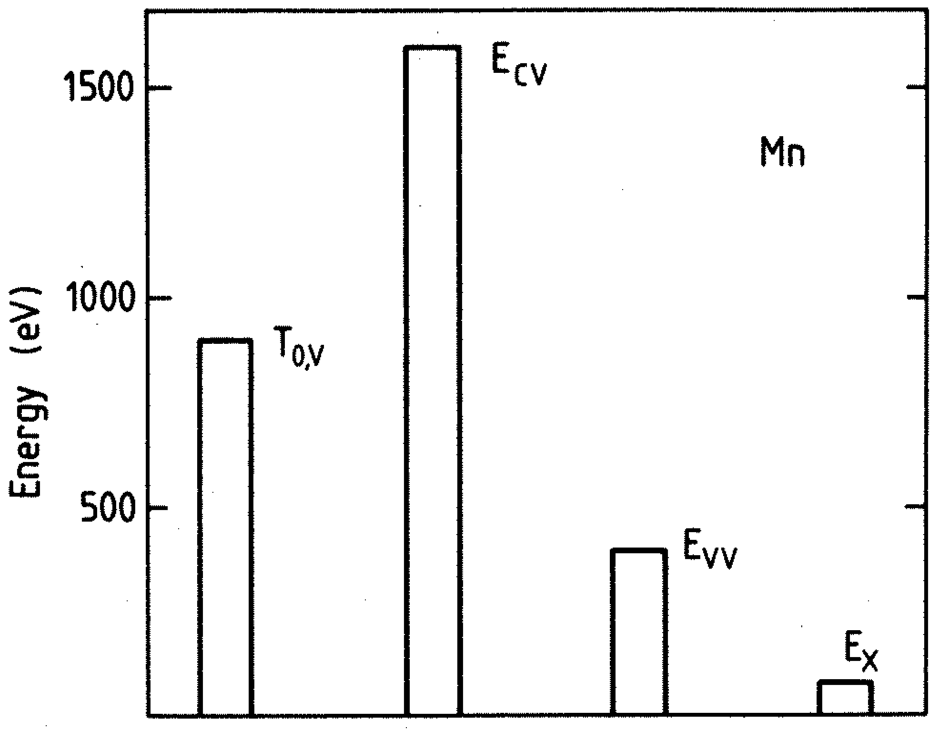
$\mathbf{R}_n$ = atomic position.

- Phonon frequencies, surface reconstructions, catalysis, ...



The Local Density Approximation works since ...

- Only a small part of the total energy is approximated.



Hartree (E_{CV}, E_{VV}), kinetic ($T_{0,\mathrm{V}}$) and exchange (E_{X}) contributions to total valence energy of Mn atom.

Correlation energy $E_{\mathrm{C}} \approx 0.1 E_{\mathrm{X}}$

The Local Density Approximation works since ...

- Errors in the approximation of exchange and correlation cancel (e.g., in atoms: 10% error in E_x partially compensated by 100-200% error in E_c).

- LDA does fulfill the sum rule for the exchange-correlation hole

$$\int d\mathbf{r}' n_{xc}(\mathbf{r}, \mathbf{r}' - \mathbf{r}) = -1$$

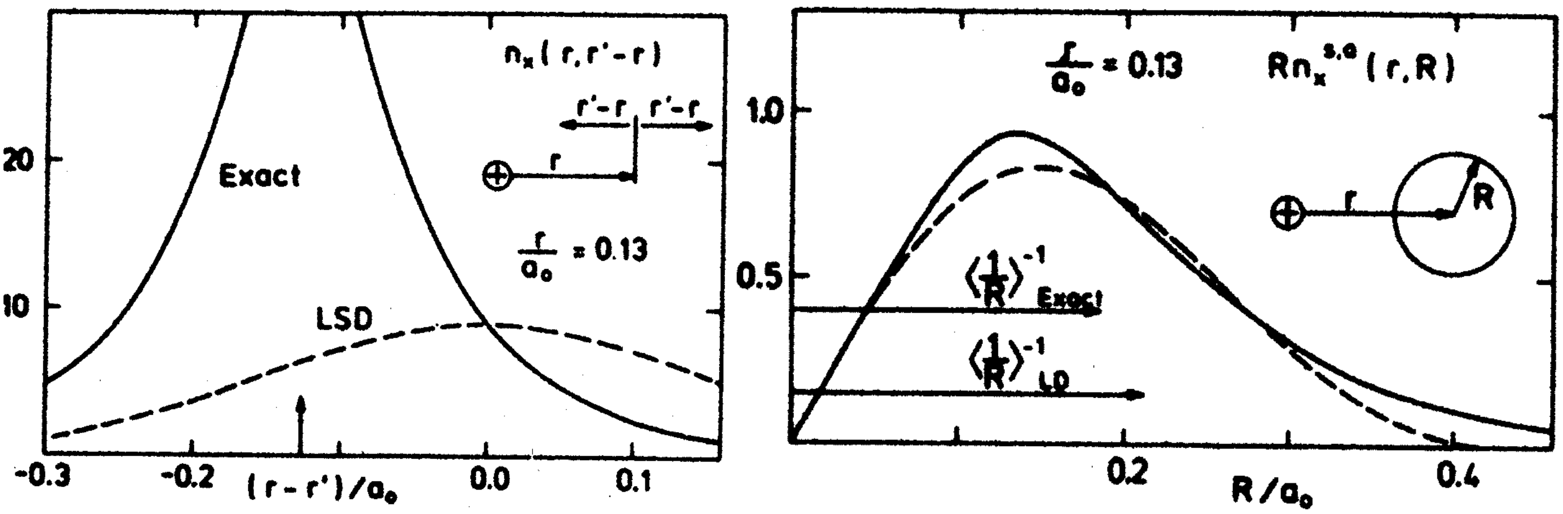
$n_{xc}(\mathbf{r}, \mathbf{r}') = n(\mathbf{r}')[\tilde{g}(\mathbf{r}, \mathbf{r}') - 1]$ = exchange-correlation hole density;

$\tilde{g}(\mathbf{r}, \mathbf{r}')$ = pair correlation function averaged over coupling constant.

- The exchange-correlation energy depends only on the angle-averaged exchange-correlation hole which is well described in LDA.

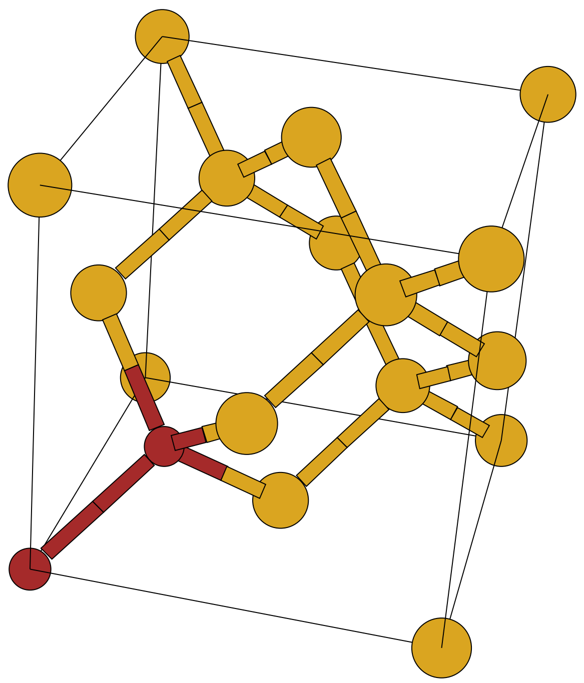
$$2E_{xc}[n] = \int \frac{n(\mathbf{r}) n_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' = \int n(\mathbf{r}) d\mathbf{r} \int \tilde{n}_{xc}(\mathbf{r}, R) dR/R,$$

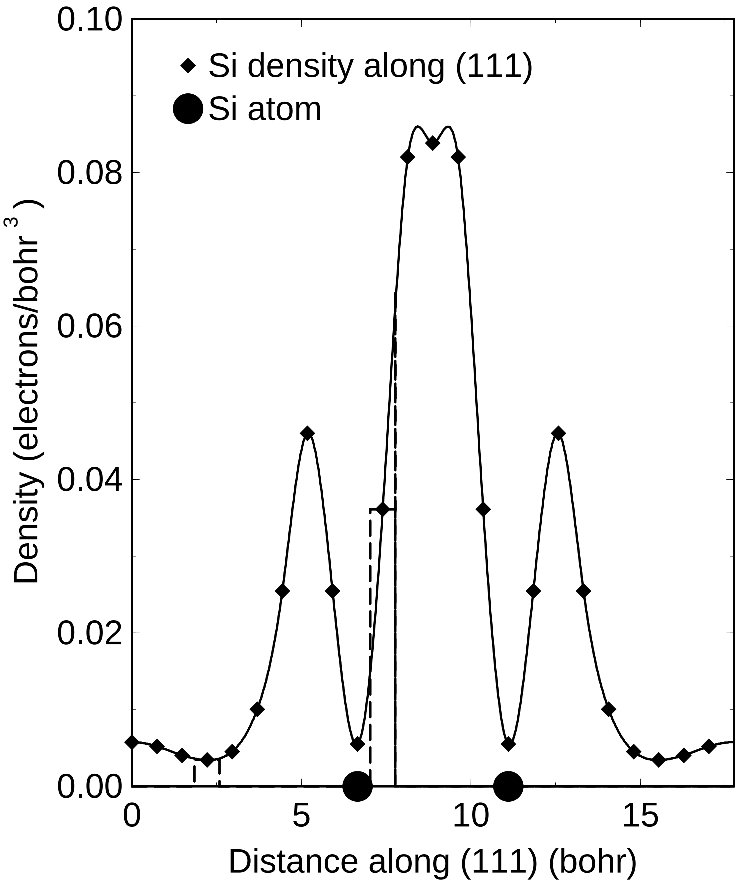
$$\tilde{n}_{xc}(\mathbf{r}, R) = \int n_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{R}) d\Omega_R / 4\pi.$$

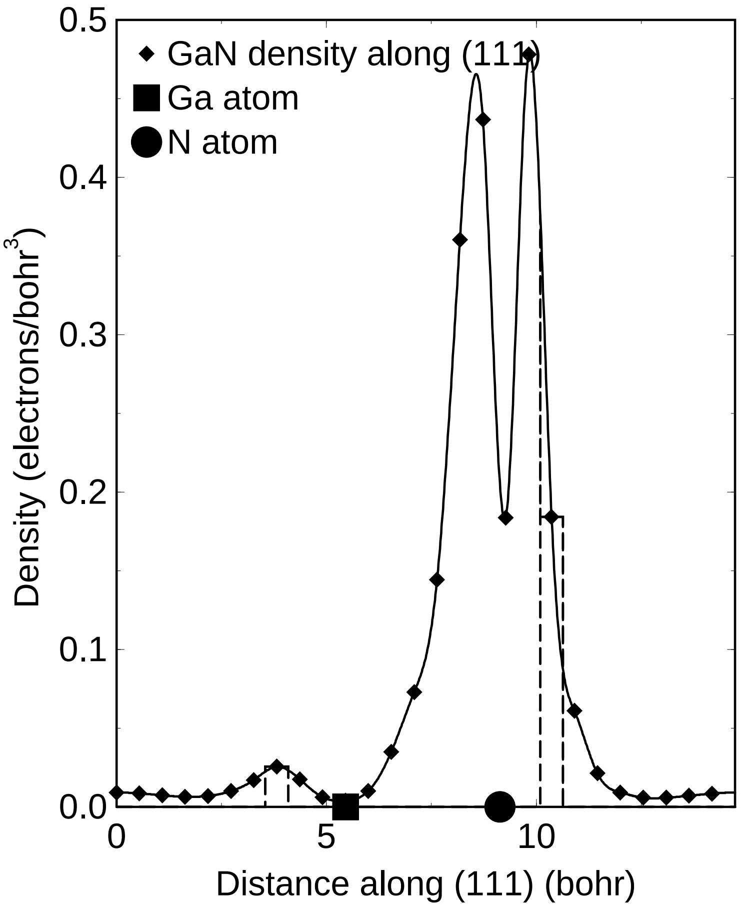


X-hole for spin-up nitrogen electron, r=electron-nucleus distance.

Does the density have to be slowly varying?



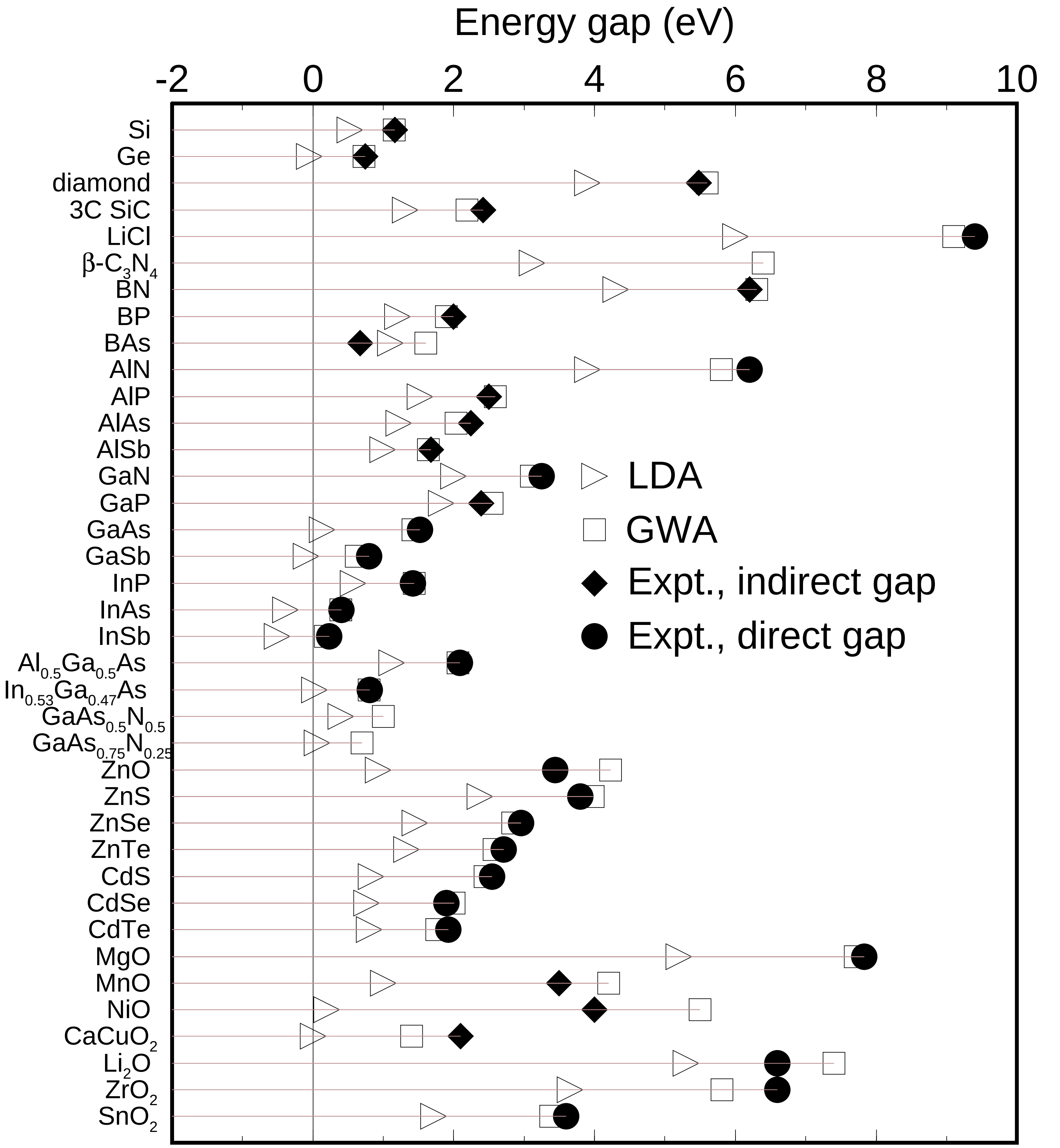




- The LDA works even if densities vary rapidly!
- The LDA is the most used approximation in DFT.

The Local Density Approximation fails for excited state properties.

- Band gaps in insulators are 0.5 to 2 eV too small (dispersion often ok).



The Local Density Approximation fails for excited state properties.

- Optical response functions too large (not a DFT failure!).

Polarization $\mathbf{P}$, macroscopic electric field $\mathbf{E}$, nth-order susceptibility $\chi^{(n)}$:

$$\mathbf{P} = \chi^{(1)}\mathbf{E} + \chi^{(2)}\mathbf{E}\mathbf{E} + \ldots$$

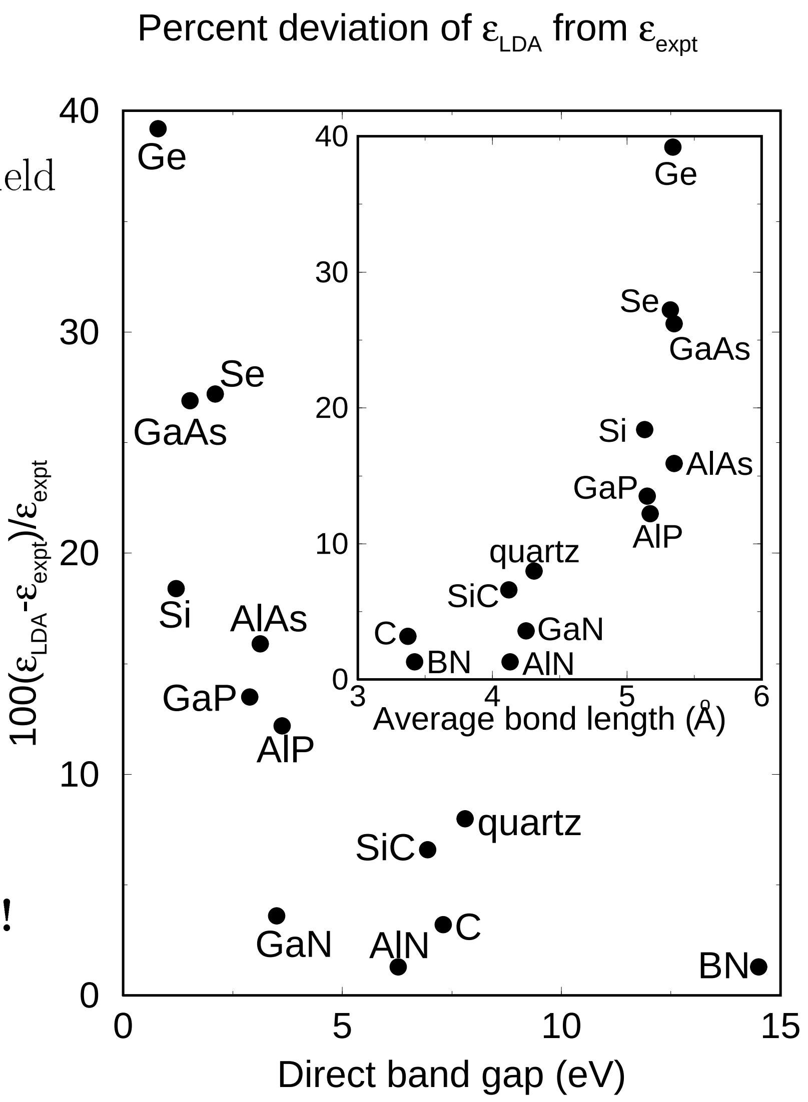
Perturbation theory:

$$\chi^{(1)} \propto \frac{|\langle \Phi_v | \mathbf{r} | \Phi_c \rangle|^2}{\varepsilon_c - \varepsilon_v}$$

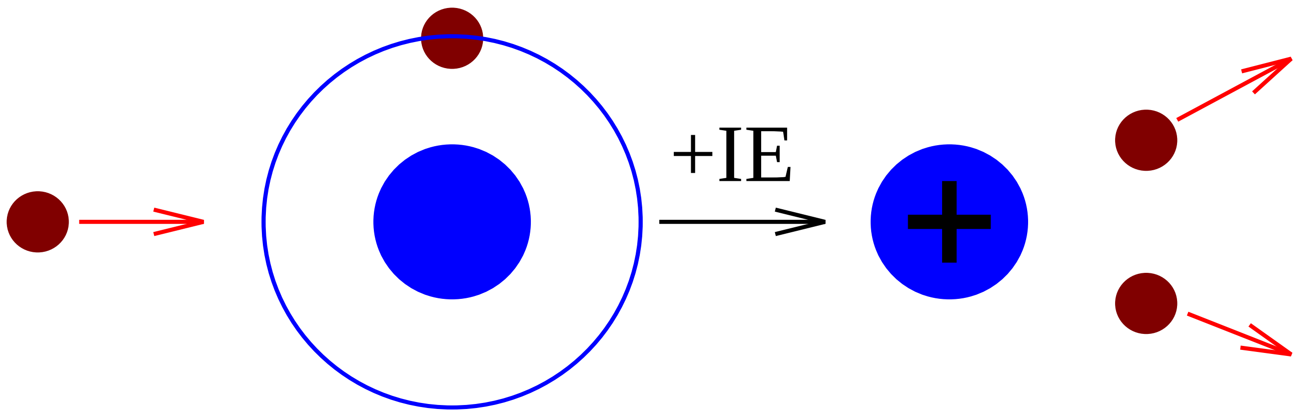
Local Density Approximation:

Wave functions ok; $\varepsilon_c - \varepsilon_v$ too small.

$\Rightarrow$ **Optical response too large!**



- Ionization energy too small by a factor of two (not a DFT failure: $\varepsilon_N = -\mathrm{IE}$).



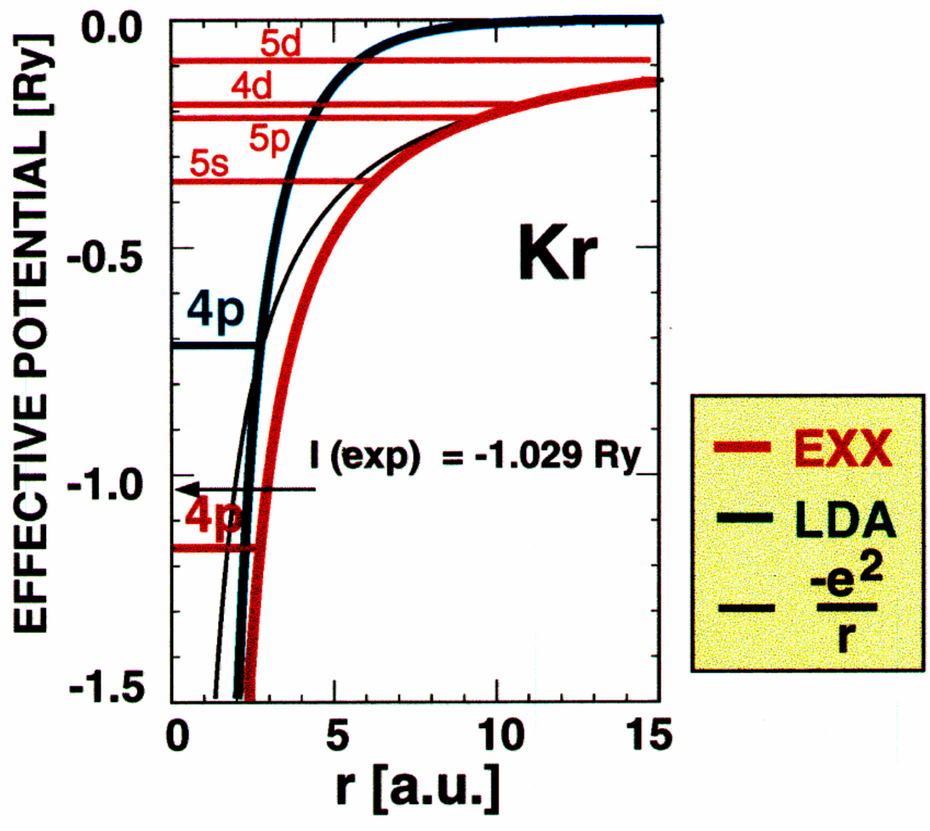
The Local Density Approximation fails since ...

- Kohn-Sham eigenvalues ε_i have no physical meaning (Lagrange param.).
- The exchange-correlation potential decays as $\exp(-\alpha r)$ rather than $-1/r$.

  – Incorrect atomic Rydberg spectra, image states at metal surfaces.

  – $-\varepsilon_N \approx 0.5$ I.

  – No integer discontinuity (insulator band gap, molecule dissociation).



- LDA self-exchange & self-Hartree potentials do not cancel.

  – Self-interaction is a 1-2 eV effect in solids.

  – Leads to wrong hybridization and relaxation since localized d and f states are underbound.

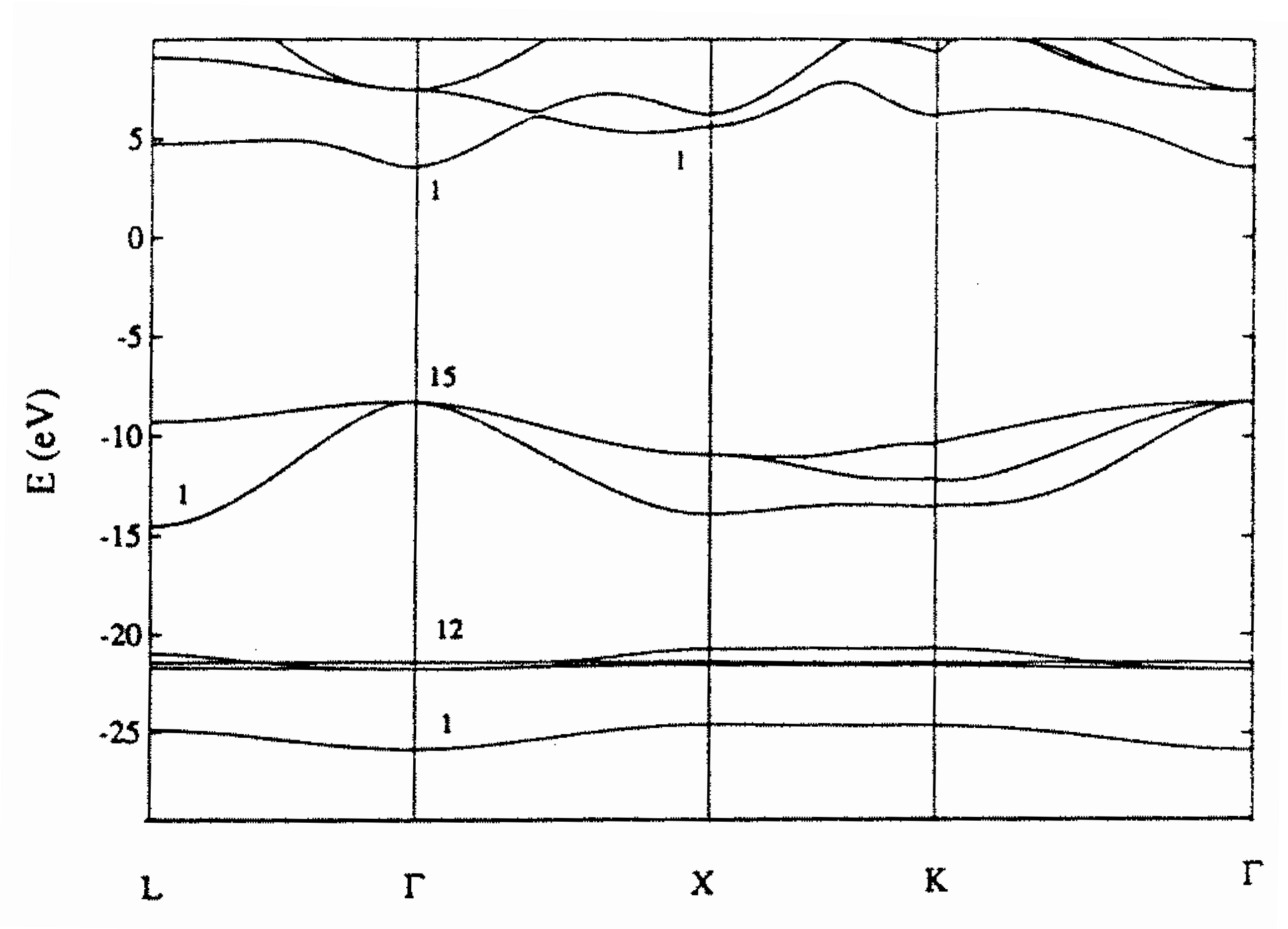
The Local Density Approximation fails since ...

- For example, self-interaction errors in Hartree-Fock:

$$\left[-\frac{\nabla^2}{2}-\frac{Z}{r}+\underbrace{\sum_j^{occ}\int\frac{|\Phi_j(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}}_{\text{Hartree}}\right]\Phi_i(\mathbf{r})-\underbrace{\sum_j^{occ}\Phi_j(\mathbf{r})\int\frac{\Phi_j^*(\mathbf{r}')\Phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'}_{\text{Exchange}}$$

Self-Hartree term cancelled by exchange only for i = occupied.

cubic ZnS



Some Extensions

- Generalized gradient approximations.

  Take the density gradient into account, particularly useful for chemistry (H-bonding).

- Spin density functional theory.

  Two independent variables: Density $n(\mathbf{r})$ and magnetization

  $$m(\mathbf{r}) = -\mu_0(n_\uparrow(\mathbf{r}) - n_\downarrow(\mathbf{r})).$$

  $m(\mathbf{r})$ couples to the magnetic field ($\alpha =\uparrow, \downarrow$):

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_H(n;\mathbf{r}) + V_{ext}(n;\mathbf{r}) - \alpha\mu_0 B(\mathbf{r}) + V_{xc}^{\alpha}(n_\uparrow, n_\downarrow;\mathbf{r})\right]\Phi_i^\alpha(\mathbf{r}) = \varepsilon_i^\alpha \Phi_i^\alpha(\mathbf{r}).$$

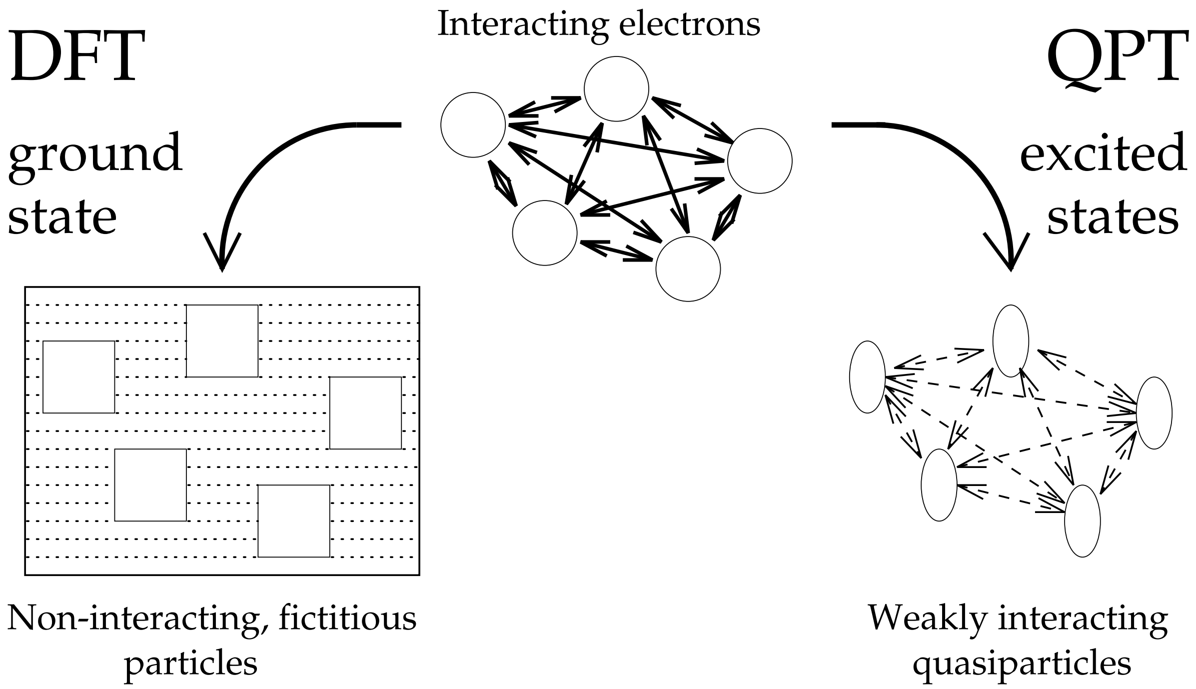
- Exact-exchange density functional theory.

  Determine exchange exactly and approximate correlation, e.g., as a functional of density. Obtain better energy gaps and fair structural properties.

- Generalized density functional theory.

  Modify Kohn-Sham energy partitioning to obtain a non-local Hamiltonian.

An Alternative: Green Functions



Kohn-Sham equation

$$\left[\hat{T} + \hat{V}_H \ + \ \hat{V}_{ext} + \hat{V}_{xc}\right]\Phi_i = \varepsilon_i \Phi_i$$

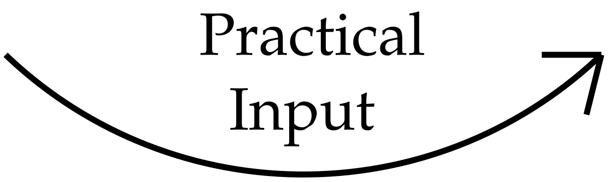
$$n(\mathbf{r}) \ = \ \sum_i |\Phi_i(\mathbf{r})|^2$$

- Works for structural properties.
- Fails for energy gap.
- V_{xc}: local, energy-independent, Hermitian (LDA).
- Self-consistent density.

Quasiparticle equation

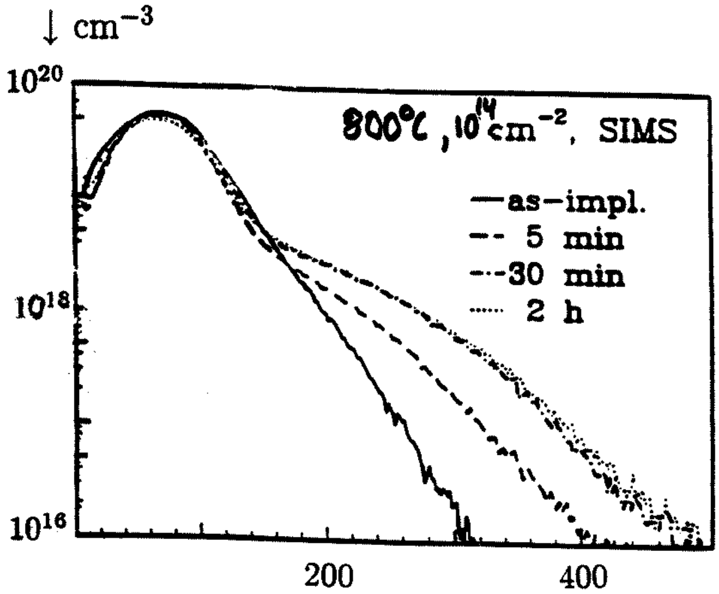
$$\left[\hat{T} + \hat{V}_H + \hat{V}_{ext}\right]\Psi_i \ + \ \int \Sigma(\mathbf{r}, \mathbf{r}'; E_i)\Psi_i(\mathbf{r}')d\mathbf{r}' \ = \ E_i \Psi_i$$

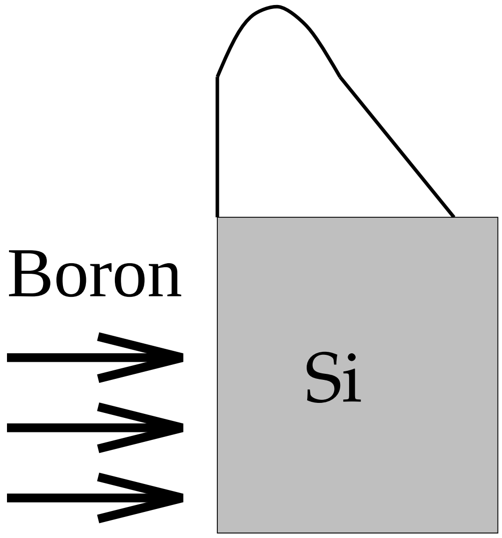
- Unproven for structure.
- Works for excitation energies.
- Σ: non-local, energy-dependent, non-Hermitian.
- Self-consistent energy.

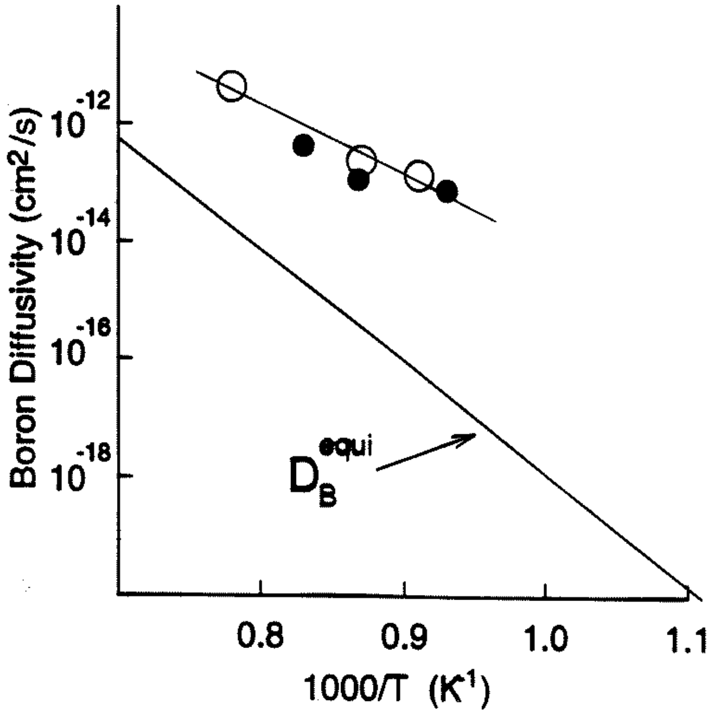


Current Topics: Defected Materials: Si

- Ion implantation of boron in Si: *p*-type doping of Si chips.
- Upon annealing diffusion coefficient at least 10^2 times larger than in bulk: **Transient enhanced diffusion** limits chip size.
- Si interstitial clusters & extended defects responsible: How do they form?
- What is the connection between interstitials & extended defects?





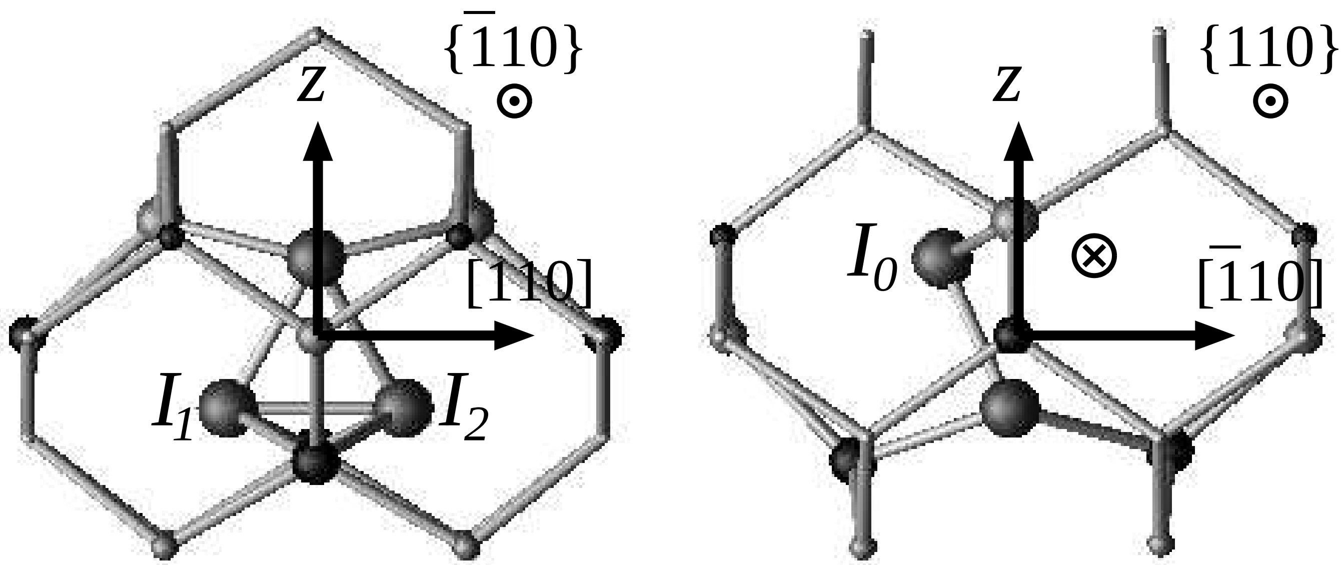


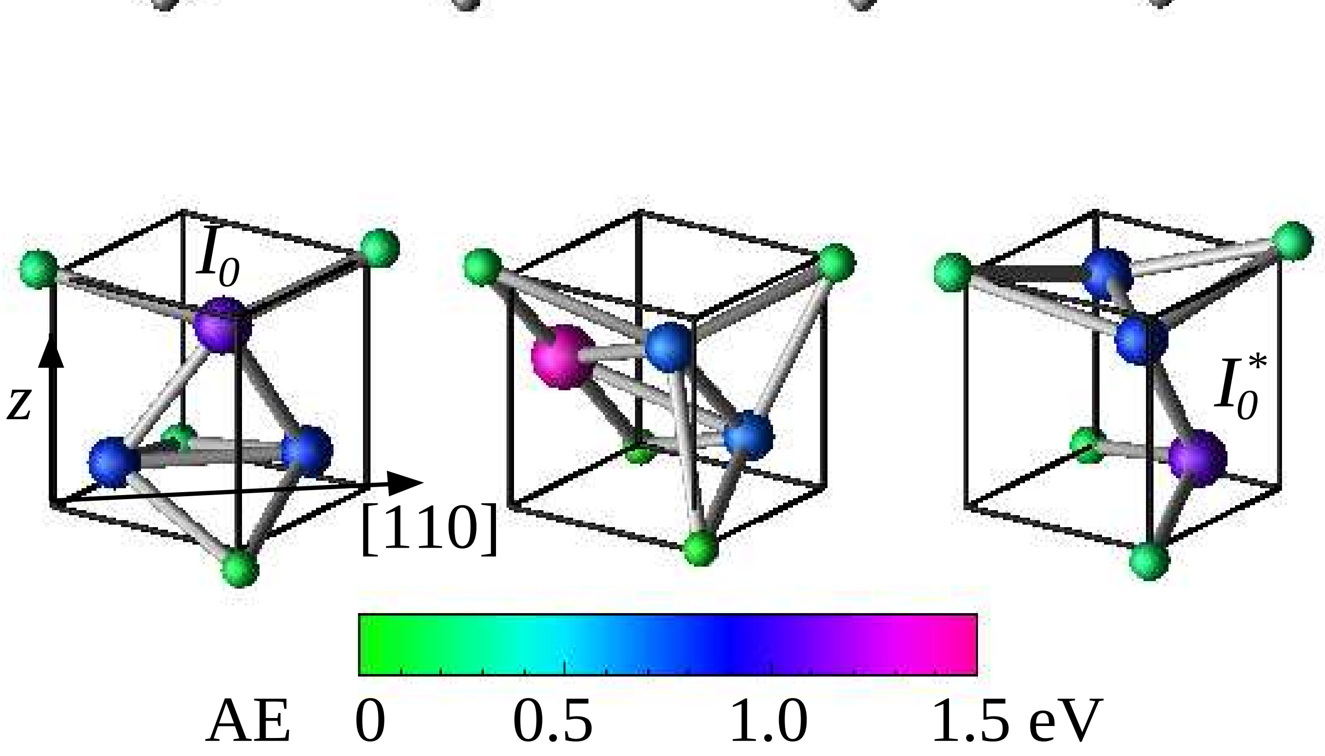
Current Topics: Defected Materials: Si

Kim *et al.*:

- Stability hierarchy: increasing binding energy for interstitial clusters $\rightarrow$ interstitial chains $\rightarrow$ two-dimensional defects.

- Activated behavior for Si P6 center: low-T C_{1h} $\rightarrow$ high-T D_{2d}.



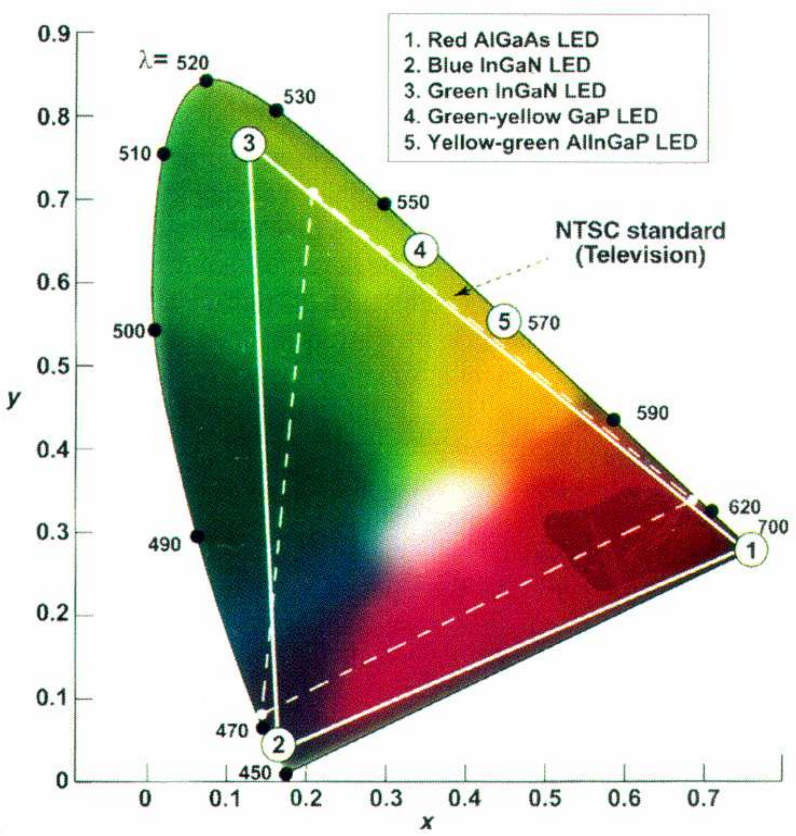


Current Topics: Defected Materials: GaN

Blue GaN-based Light-Emitting Diodes (Nakamura *et al.*).

- Better color than TV.
- 80-90% less energy consumption than light bulbs.
- 10 × longer life time than light bulbs.
- 10^6 × more defects than in GaAs-based devices.

Why do GaN LEDs & lasers work?



Quantitative theory of

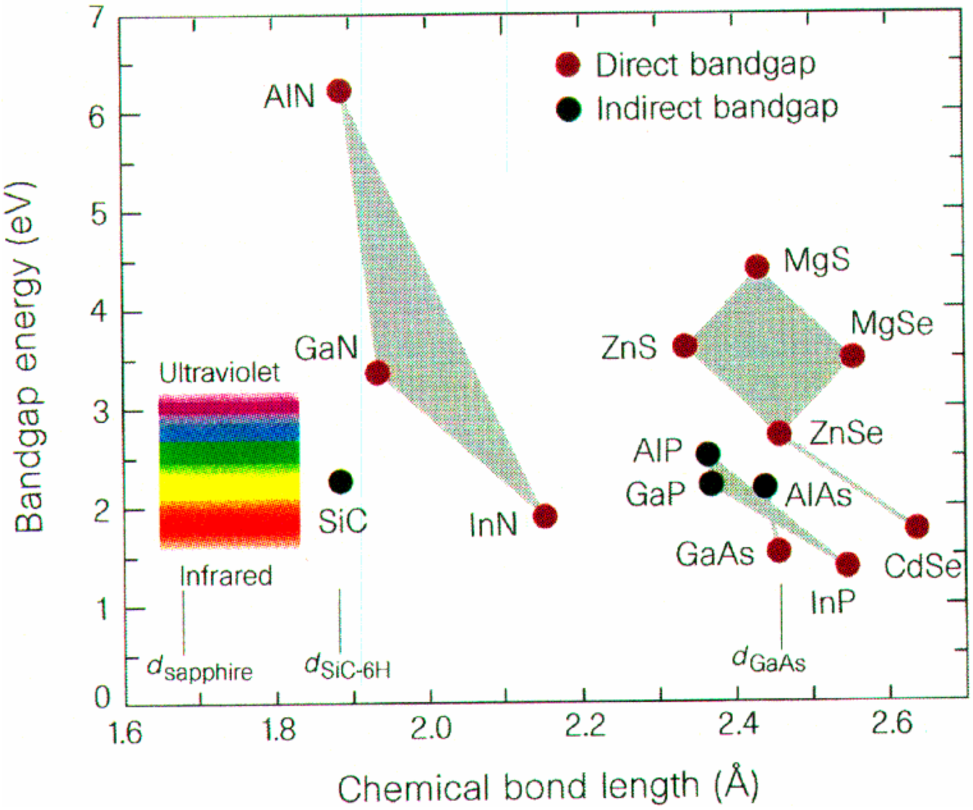
- atomic and electronic structure of defects (vacancies, edge and screw dislocations, etc.), and
- transport properties of superlattices (valence band off-sets, effective masses)

needed to predict device performance.

For example, **quasiparticle calculations** increase LDA by 30%:

	standard	quasiparticle	experiment
valence band off-set	**0.8** eV	**1.2** eV	**1.2** eV

Fig. 11. The actual LED traffic light which was set in Berlin, Germany in 1996 using InGaN SQW green, AlInGaP yellow and AlInGaP red LEDs.



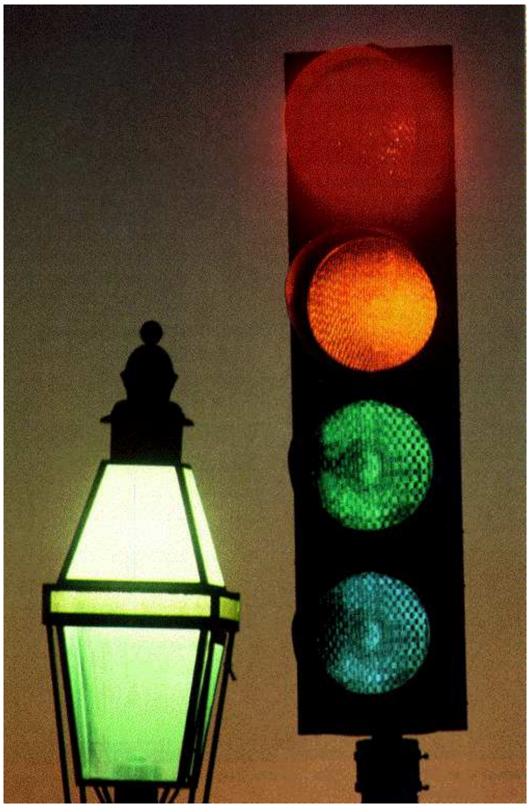
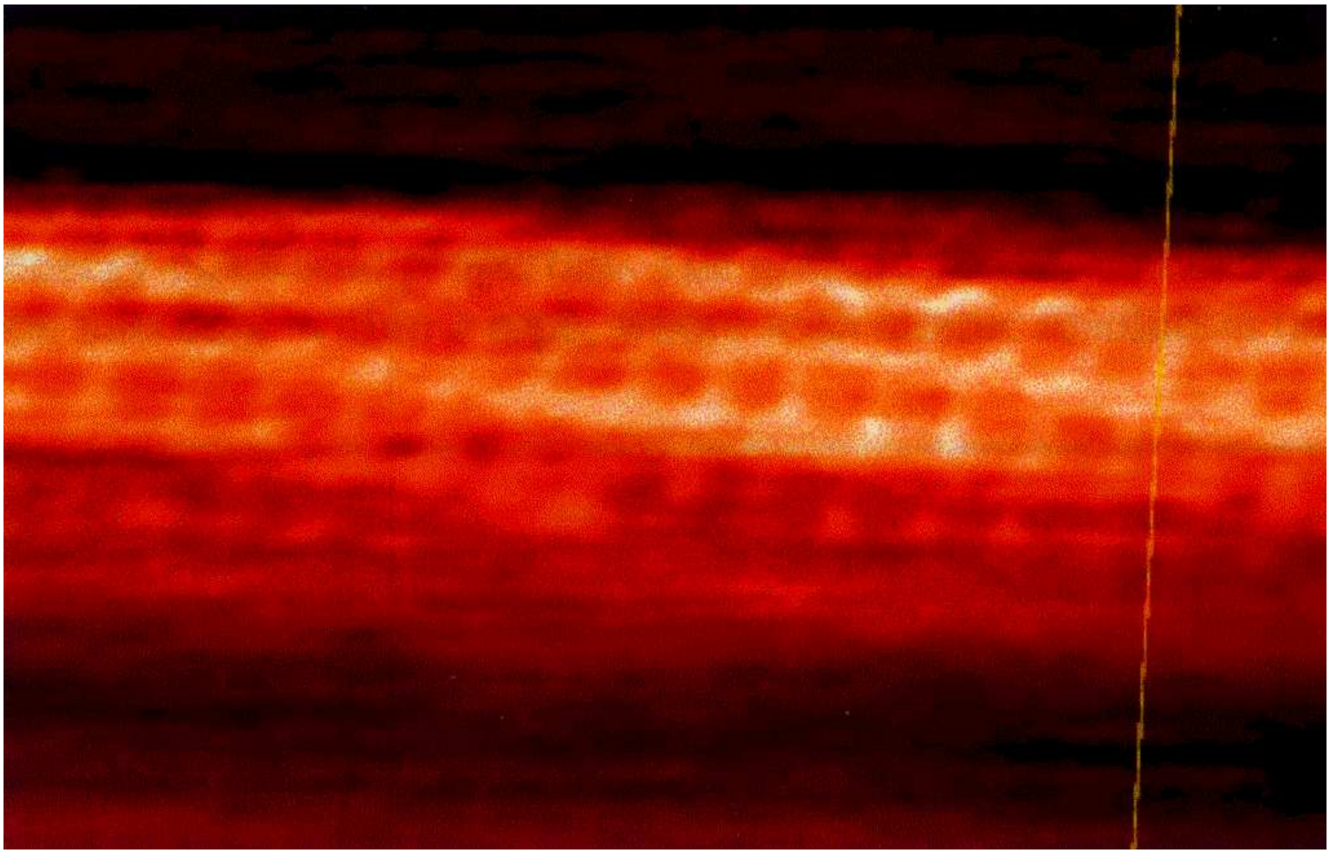


Fig. 12. The actual LED full-color display which was set up in Japan in 1996. The blue InGaN SQW LEDs, green InGaN SQW LEDs and red GaAlAs LEDs are used as three primary color LEDs.

Current Topics: Nanotubes

- Carbon nanotubes are rolled up graphite sheets (single-, multi-walled, ropes) with nanometer-scale diameters and micrometer length.
- Predicted to be metals, semiconductors, insulators depending on chirality (metal-semiconductor junctions, *pn* junctions $\Rightarrow$ nano-electronics).
- Predicted to be very elastic.
- Method: Density functional theory & tight-binding.
- Example: Structural flexibility of carbon nanotubes.



Johnson *et al.*, University of Pennsylvania, STM

Current Topics: Nanotubes

Theory (Bernholc *et al.*)

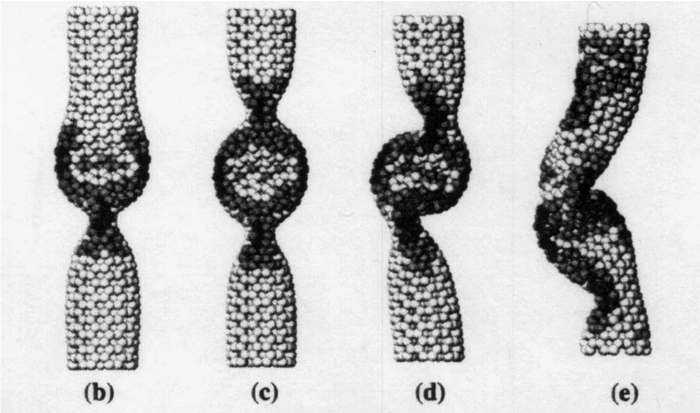


FIG. 1. MD-simulated nanotube of length $L = 6$ nm, diameter $d = 1$ nm, and armchair helicity (7,7) under axial compression. The strain energy (a) displays four singularities

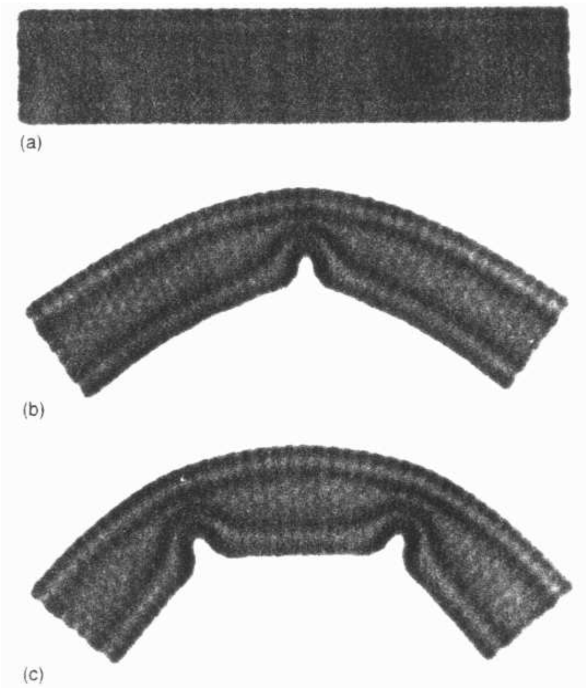


FIG. 4. Simulated cross-sectional images of a double-walled tube (diameters 1.0 and 1.7 nm) under a progressively increased bending: (a) the straight relaxed tube; (b) a single kink forming above a critical curvature; and (c) a two-kink complex forming in the middle at large bending. The distance between the two kinks (~ 2 nm) was found to be constant over a wide range of bend angles.

Experiment (Lourie *et al.*, TEM)

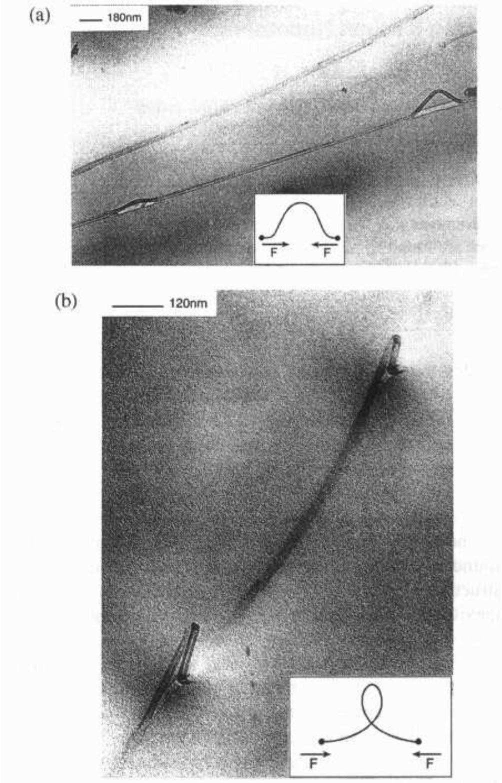


FIG. 1. TEM micrographs of long and slender multiwall carbon nanotubes which, under compression, behave as elastica rods and form bends (a) and loops (b).

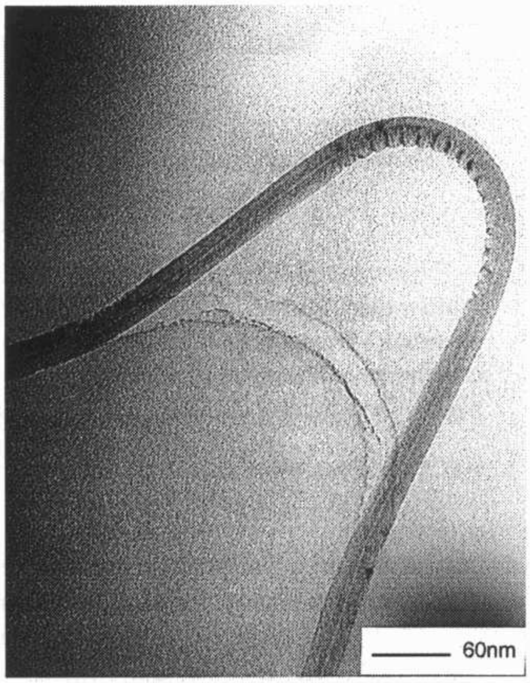


FIG. 2. Under high bending, nanotubes collapse to form kinks on the internal (compression) side of the bend, which fits the predictions of Refs. [2,8].

Current Topics: Proteins

- Determination of chemical reactions, catalysis, etc. (energy, intermediate products).
- Explore atomic and electronic structure of proteins which determine protein functionality.
- Generalized gradient approximation more accurate than LDA.
- Example: Solution of amyloid β-peptide ($C_{146}O_{45}N_{42}H_{210}$) in water $\Rightarrow$ Alzheimer's disease.

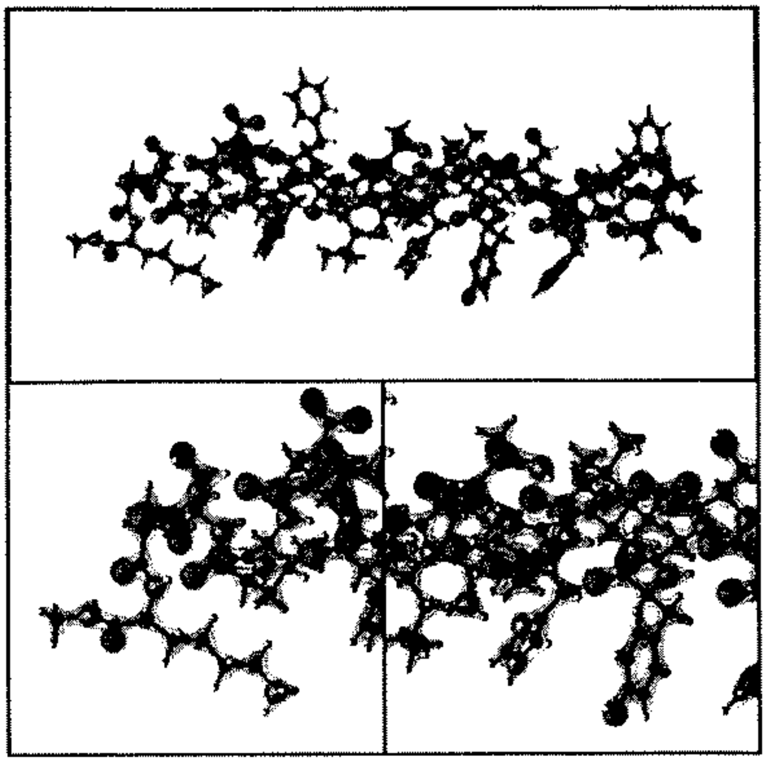


FIGURE 10. Three views of the electronic charge density of the amyloid β-peptide associated with Alzheimer's disease. The top view shows the entire molecule; the lower two views are close-ups of the first quarter and second third of the molecule, respectively.

- Example: Protein nanotubes.

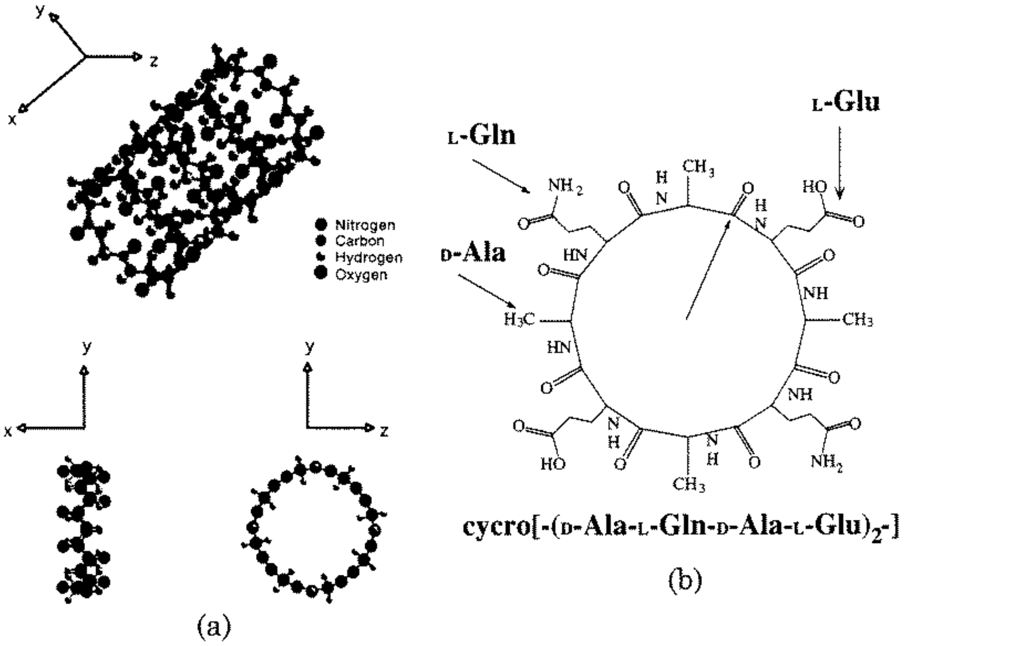


Fig. 1. Overviews of Gly-NTB (a) and molecular structure of a CPR subunit ring (b). All amino-residues of Ala, Gln, and Glu are replaced by Gly in the present calculation.

Conclusions: Kohn (1998)

- Density functional theory is one of the most powerful tools in theoretical/computational condensed matter physics (more than 4000 citations of original papers in last 9 years).
- Exciting and continuous progress on the level of theory, algorithms, and applications will continue in the future.
- The future looks bright: Major impacts in material science, biology, physics of correlation, etc., are to be expected.
- A word of caution: Credible determination of material properties (cancellation of different pieces of physics).