The electronic structure of solids:

Band structure, Density of States, Fermi-Surfaces and Charge Densities

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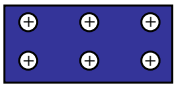
Free Electron Gas

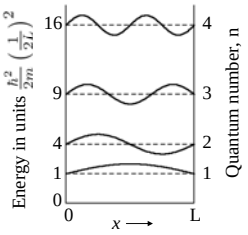


schematic model of a monovalent metal

1D: $h\psi_n = -\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} = \epsilon_n\psi_n$

$\psi_n = A\sin\left(\frac{n\pi}{L}x\right)$

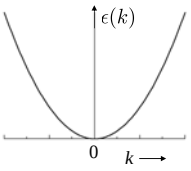
$\epsilon_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2$



3D: $-\frac{\hbar^2}{2m}\nabla^2\psi_{\mathbf{k}}(\mathbf{r}) = \epsilon_{\mathbf{k}}\psi_{\mathbf{k}}(\mathbf{r})$

$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}}$

$\epsilon_{\mathbf{k}} = \frac{\hbar^2}{2m}\mathbf{k}^2$



Free Electron Gas

+ describes many physical properties of metals:

- heat capacity
- thermal conductivity
- electrical conductivity
- magnetic conductivity
- electrodynamics

- but fails to describe:

- distinction between metals, semimetals, semiconductors and insulators
- many transport properties

Nearly Free Electron Gas

Electron in a periodic potential: $v^{\text{eff}}(\mathbf{r}+\mathbf{R}_n) = v^{\text{eff}}(\mathbf{r})$

$\mathbf{R}_n$ ≡ translational lattice vector: $\mathbf{R}_n = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$

$$h\psi_{\mathbf{k}}(\mathbf{r}) = \left(-\frac{\hbar^2}{2m}\nabla^2 + v^{\text{eff}}(\mathbf{r})\right)\psi_{\mathbf{k}}(\mathbf{r}) = \epsilon_{\mathbf{k}}\psi_{\mathbf{k}}(\mathbf{r})$$

Bloch theorem:

=> Solution of the Schrödinger equation for a periodic potential

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}}u_{\mathbf{k}}(\mathbf{r}) \qquad \text{with} \qquad u_{\mathbf{k}}(\mathbf{r}+\mathbf{R}_n) = u_{\mathbf{k}}(\mathbf{r})$$

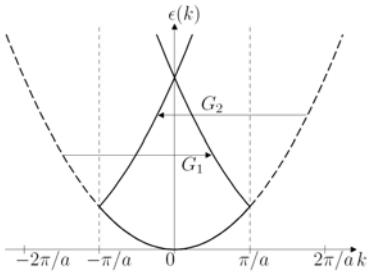
$$\psi_{\mathbf{k}}(\mathbf{r}+\mathbf{R}_n) = e^{i\mathbf{k}\mathbf{R}_n}\psi_{\mathbf{k}}(\mathbf{r})$$

Once the plane wave is modulated by the lattice, there is no single "true" wavevector for the state ψ

Empty Lattice Approach

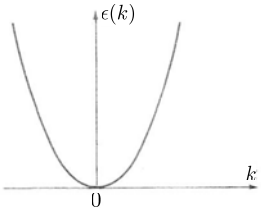
Energies in a very weakly varying potential:

$\epsilon_n(\mathbf{k}) \approx \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{G}_n)^2$ **with** $\mathbf{G}_n = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3$

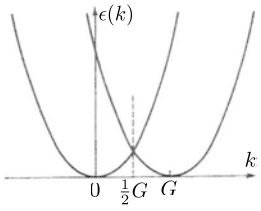


Distortion in the Free Electron Parabola

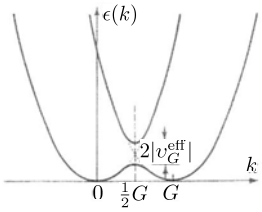
free electron

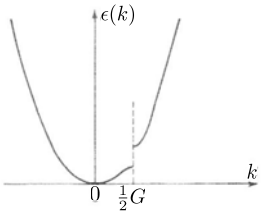


bloch electron



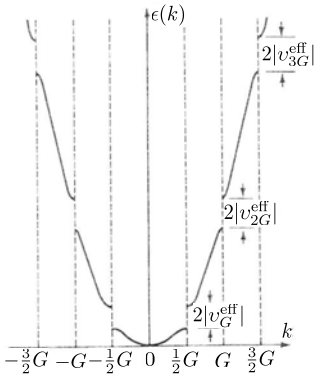
distortion due to a weak periodic potential



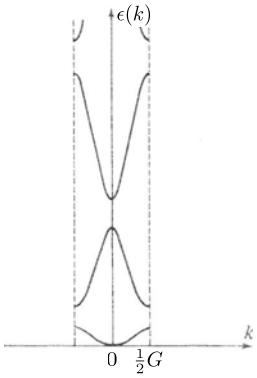


Different Zone Schemes

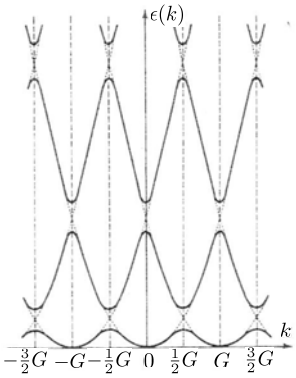
extended-zone scheme



reduced-zone scheme

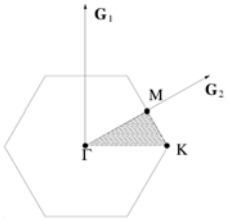


repeated-zone scheme



Hexagonal Lattice in 2D

2D Brillouin zone



$\mathbf{G}_0 = (0,0) = \Gamma$

$\mathbf{G}_1 = \frac{2\pi}{a}(0,1)$

$\mathbf{G}_2 = \frac{2\pi}{a}(\frac{\sqrt{3}}{2}, \frac{1}{2})$

e.g. direction:

$\Gamma \rightarrow \mathrm{K} = \overline{\Gamma\mathrm{K}}$

$\Gamma = (0,0)$, $\mathrm{K} = \frac{2\pi}{a}(\frac{1}{\sqrt{3}}, 0)$

$\mathbf{k} = (k_x, 0)$

Energy

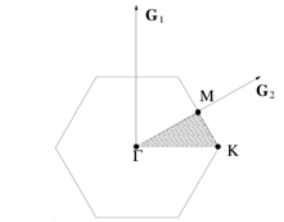
$$\epsilon_n(\mathbf{k}) = \frac{\hbar^2}{2m}(\mathbf{k} + \mathbf{G}_n)^2$$

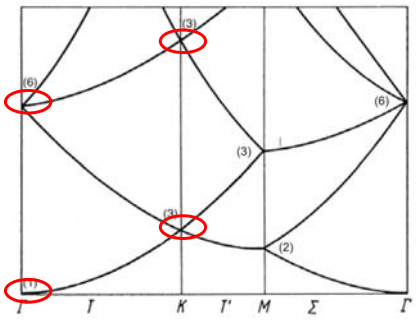
Energybands

$$\begin{aligned}
\mathbf{G}_0: \quad \epsilon_0(\mathbf{k}) &= \tfrac{\hbar^2}{2m}k_x^2 \\
\epsilon_0(\Gamma) &= 0 \\
\epsilon_0(\mathrm{K}) &= \tfrac{\hbar^2}{2m}(\tfrac{2\pi}{a}\tfrac{1}{\sqrt{3}})^2 \\
\mathbf{G}_1: \quad \epsilon_1(\mathbf{k}) &= \tfrac{\hbar^2}{2m}(k_x^2 + (\tfrac{2\pi}{a})^2) \\
\epsilon_1(\Gamma) &= \tfrac{\hbar^2}{2m}(\tfrac{2\pi}{a})^2 \\
\epsilon_1(\mathrm{K}) &= \tfrac{\hbar^2}{2m}(\tfrac{1}{3}+1)\cdot(\tfrac{2\pi}{a})^2
\end{aligned}$$

etc.

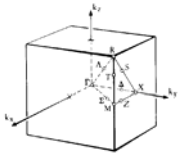
Hexagonal Lattice in 2D



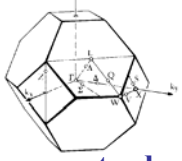


$$
\begin{aligned}
\mathbf{G}_0: \quad \epsilon_0(\mathbf{k}) &= \tfrac{\hbar^2}{2m}k_x^2 \\
\epsilon_0(\Gamma) &= 0 \\
\epsilon_0(\mathrm{K}) &= \tfrac{\hbar^2}{2m}(\tfrac{2\pi}{a}\tfrac{1}{\sqrt{3}})^2 \\
\mathbf{G}_1: \quad \epsilon_1(\mathbf{k}) &= \tfrac{\hbar^2}{2m}(k_x^2 + (\tfrac{2\pi}{a})^2) \\
\epsilon_1(\Gamma) &= \tfrac{\hbar^2}{2m}(\tfrac{2\pi}{a})^2 \\
\epsilon_1(\mathrm{K}) &= \tfrac{\hbar^2}{2m}(\tfrac{1}{3}+1)\cdot(\tfrac{2\pi}{a})^2 \\
\mathbf{G}_2: \quad \epsilon_2(\mathbf{k}) &= \tfrac{\hbar^2}{2m}(k_x^2 + \tfrac{2\pi}{a}\tfrac{\sqrt{3}}{2})^2 + (\tfrac{2\pi}{a})^2\cdot\tfrac{1}{4} \\
\epsilon_2(\Gamma) &= \tfrac{\hbar^2}{2m}(\tfrac{2\pi}{a})^2(\tfrac{3}{4}+\tfrac{1}{4}) \\
&= \tfrac{\hbar^2}{2m}(\tfrac{2\pi}{a})^2 = \epsilon_1(\Gamma) \\
\epsilon_2(\mathrm{K}) &= \tfrac{\hbar^2}{2m}(\tfrac{2\pi}{a})^2\cdot\tfrac{7}{3} \\
\mathbf{G}_3: \quad &\ldots
\end{aligned}
$$

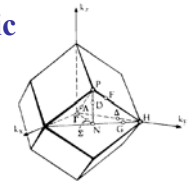
3D Brillouin Zones



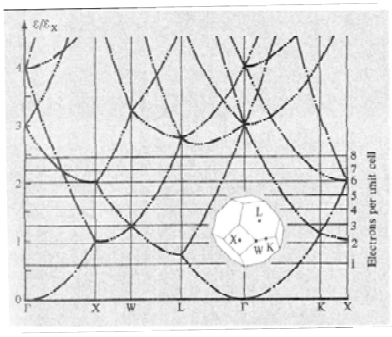
simple cubic

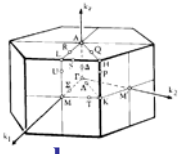


face-centred cubic



body-centred cubic

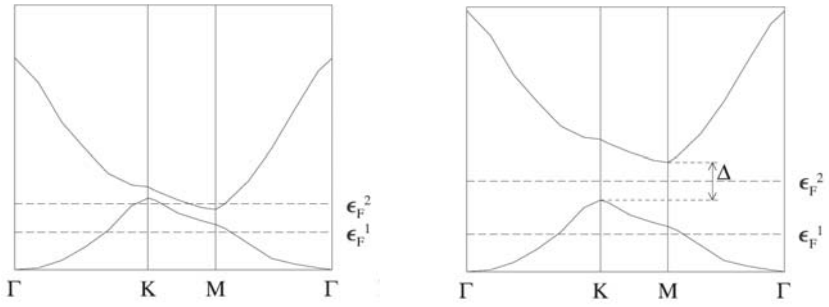




hexagonal

What can we learn from a Band Structure

$\Delta < 0$ $\qquad$ $\Delta > 0$

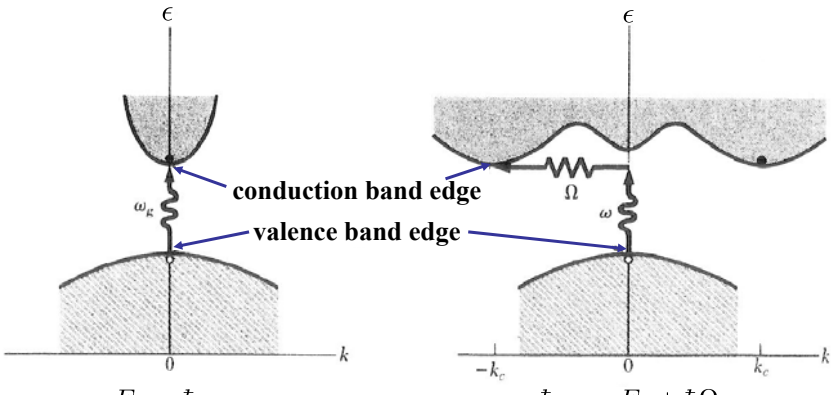


$\epsilon_F^1 \equiv$ **One electron per cell**

$\epsilon_F^2 \equiv$ **Two electrons per cell**

Direct and Indirect Band Gap

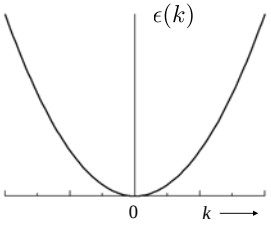
direct band gap $\qquad$ **indirect band gap**



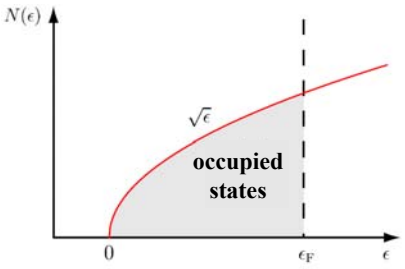
$E_g = \hbar\omega_g$ $\qquad$ $\hbar\omega_g = E_g + \hbar\Omega$

Density of States

3D Free electron gas:



$$\epsilon_{\mathbf{k}} = \frac{\hbar^2}{2m}\mathbf{k}^2$$



$$N(\epsilon) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{2/3}\sqrt{\epsilon}$$

In general:

$$N(\epsilon) = \sum_n \frac{2}{(2\pi)^3}\int_{1.\mathrm{BZ}} \delta(\epsilon - \epsilon_n(\mathbf{k}))d^3k$$

Examples: Copper

Electronic configuration: $1s^2\ 2s^2\ 2p^6$ $3s^2\ 3p^6$ $3d^{10}\ 4s^1$

core semicore valence

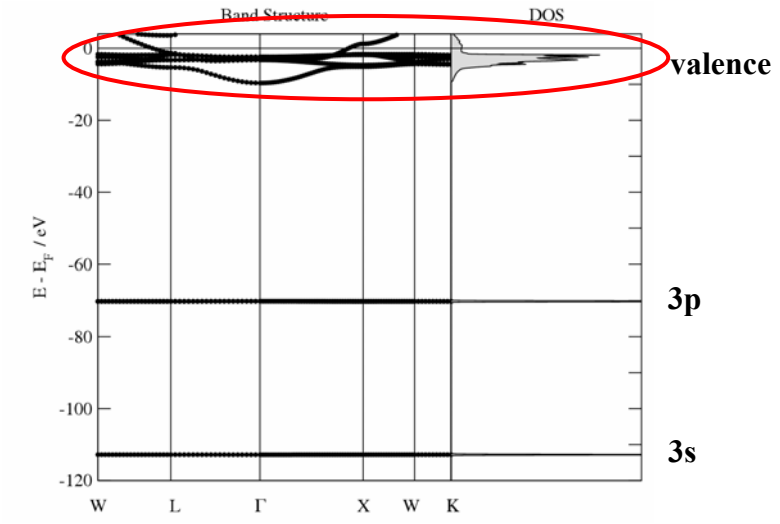
semicore and valence
2s 2p

core states show no dispersion

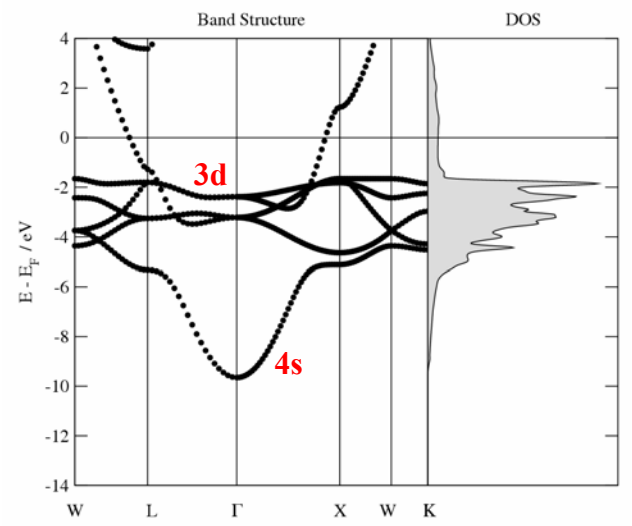
=> very localized

1s

Copper: Semicore and Valence States

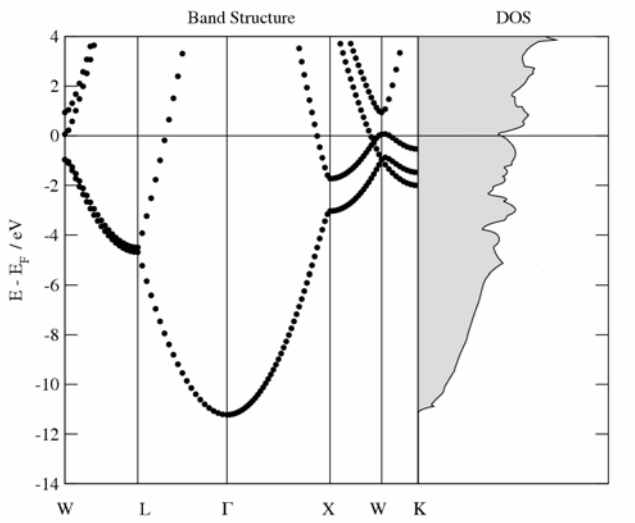


Copper: Valence States



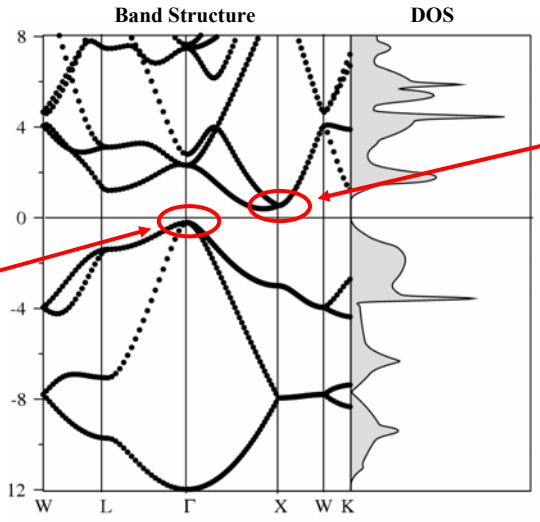
Aluminium: Valence States

Electronic configuration: $1s^2\ 2s^2\ 2p^6$ $3s^2\ 3p^1$



Silicium: Valence States

Electronic configuration: $1s^2\ 2s^2\ 2p^6$ $3s^2\ 3p^2$



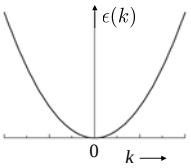
top of the valence band

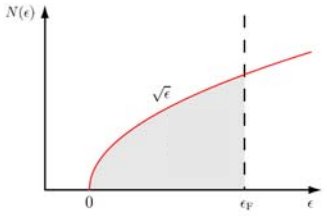
bottom of the conduction band

indirect band gap !!

Fermi Surfaces

3D Free electron gas:



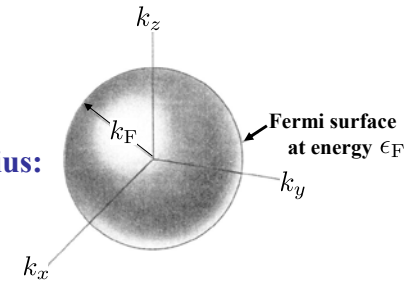


Surface of constant energy in reciprocal space: $\epsilon(k) = \epsilon_F$

=> only in metals!

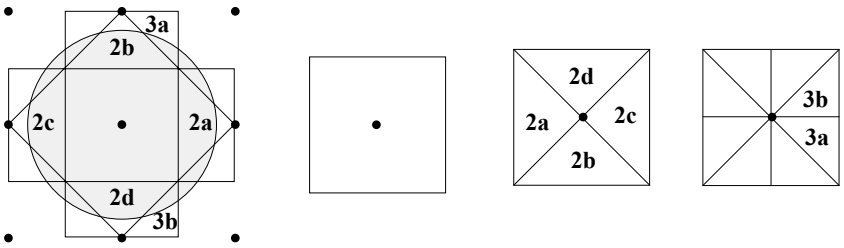
=> determines electrical properties

Fermi Surface is a sphere with radius:

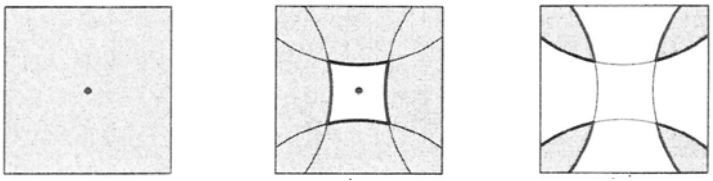


2D Fermi Surface: empty lattice

2D Fermi "circle":

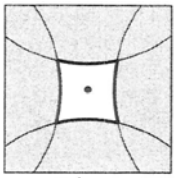


1st zone **2nd zone** **3rd zone**

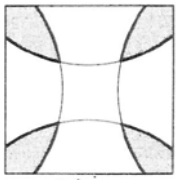


Distorting the Fermi Surface

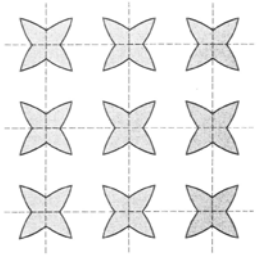
2nd zone



3rd zone

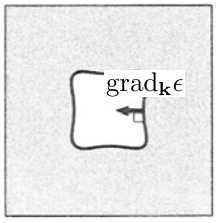


3rd zone in periodic zone scheme

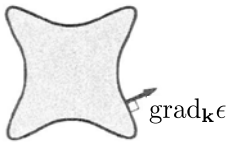


Distortion due to weak periodic potential

2nd zone

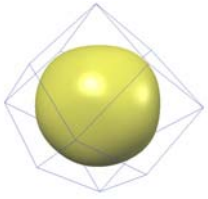


3rd zone



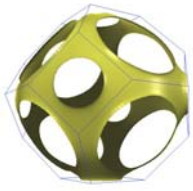
3D Fermi Surface

1 valence e^-



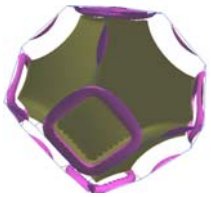
Na

2 valence e^-



Ca

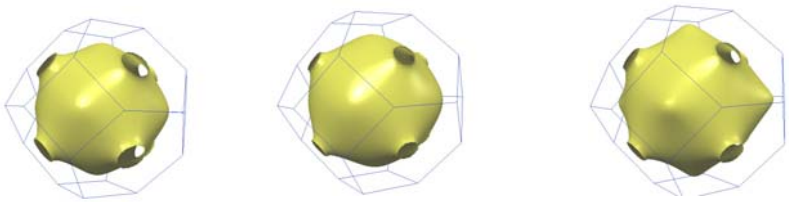
3 valence e^-



Al

web page: http://www.phys.ufl.edu/fermisurface/

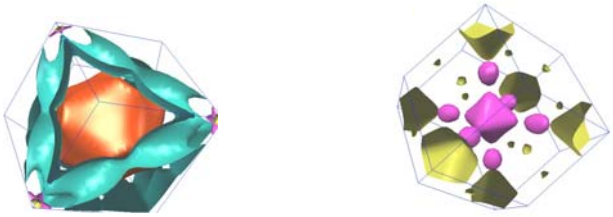
Fermi Surface: Noble Metals



Cu Ag Au

web page: http://www.phys.ufl.edu/fermisurface/

Fermi Surface: Magnetic Metals



Fe up Fe down

web page: http://www.phys.ufl.edu/fermisurface/

Charge Densities

Electronic structure in real space: $n(\mathbf{r}) = |\Psi^2|$

- **Total charge density**
- **Valence charge density**
- **Difference charge density**

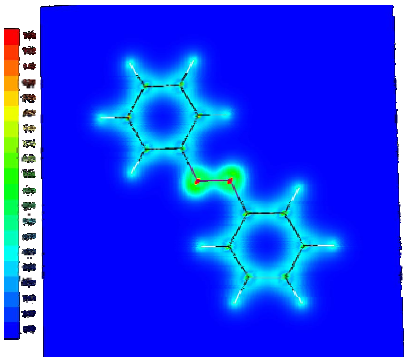
4D Information: *x,y,z* and *n*

choose a plane,
e.g. (100)
3D plot or 2D contour plot

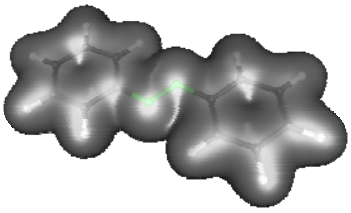
choose a density,
3D Isosurfaces

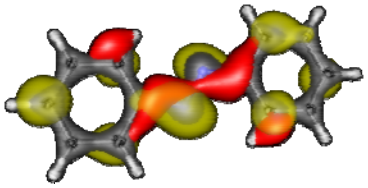
Charge Density of Azobenzene

Cutplane



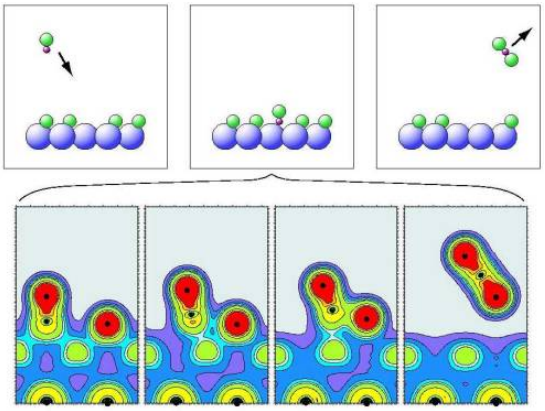
Isosurface





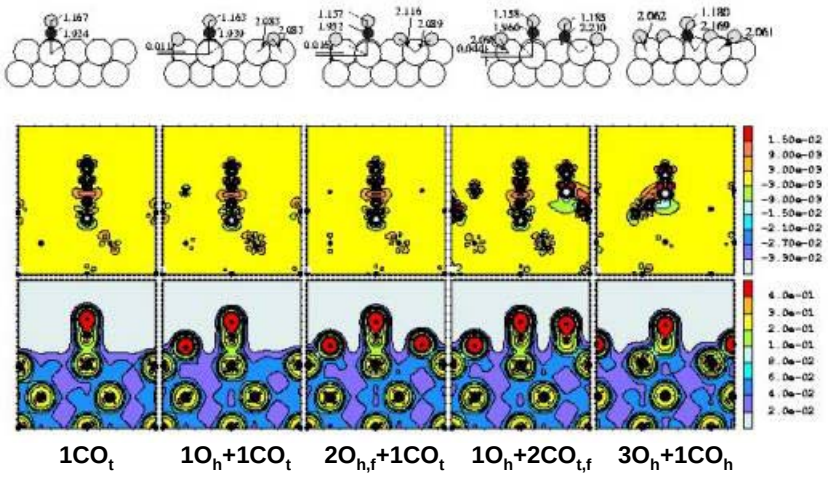
homo-lumo

CO_2 Formation on Ru(0001)



Cathy Stampfl:
http://www.physics.usyd.edu.au/~stampfl/co2-form.html

Coadsorption of O and CO on Ru(0001)



C. Stampfl and M. Scheffler, Phys. Rev. B 65, 155417 (2002).

Summary

- Electrons in a periodic potential
  ➔ Bloch wave function: $\psi_{\mathbf{k}}(\mathbf{r}+\mathbf{R}_n) = e^{i\mathbf{k}\mathbf{R}_n}\psi_{\mathbf{k}}(\mathbf{r})$
- Electrons are arranged in bands (upper and lower limit)
- Distinction between metal, semimetals, semiconductors and insulators
- Density of states ➔ integral over Brillouin zone
- Fermi surface ➔ surface of constant energy: $\epsilon(k) = \epsilon_{\mathrm{F}}$
- Charge density ➔ real space representation of electronic structure

References

N. W. Ashcroft, N. D. Mermin, "Solid State Physics", Saunders College Publishing, 1981

C. Kittel, "Introduction to Solid State Physics", John Wiley & Sons, Inc., 7th Ed. 1996

Lecture notes: M. Scheffler
http://w3.rz-berlin.mpg.de/~michaeli/member/ice3/ICE-group-teaching-page.htm