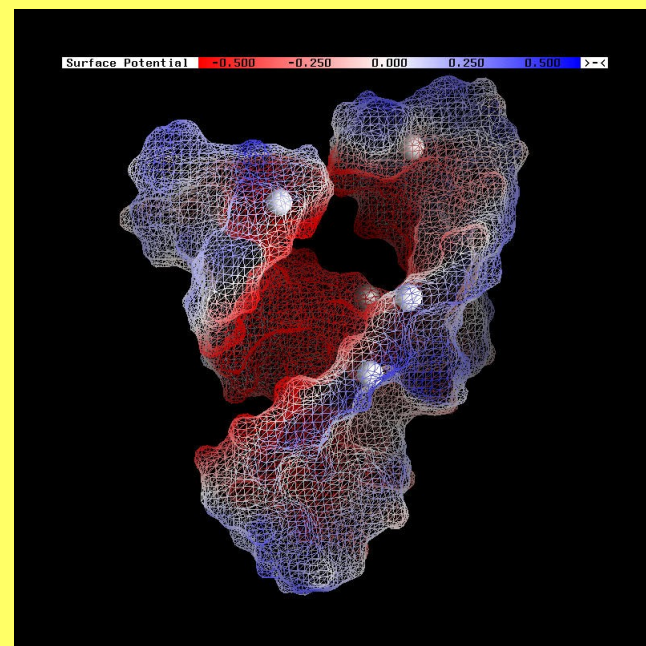
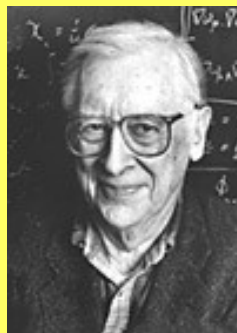
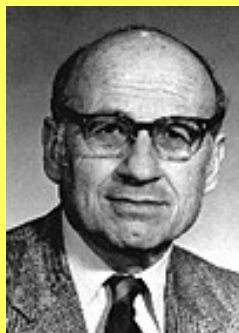


Density Functional Theory: background

- Electronic structure theory
- The electronic density
- The Hohenberg-Kohn theorems

The Nobel Prize in
Chemistry 1998

Walter Kohn and John Pople



• Electronic structure theory

- Time independent Schroedinger equation

$$\hat{H}\Psi = E\Psi$$

H : Hamiltonian operator

E : total energy of system
(eigenvalue)

Ψ : wavefunction (eigenfunction)

- The full molecular Hamiltonian

$$\hat{H} = -\frac{1}{2} \sum_{A=1}^N \frac{1}{M_A} \nabla_A^2 - \frac{1}{2} \sum_{i=1}^n \nabla_i^2 + \sum_{A<B} \frac{Z_A Z_B}{R_{AB}} + \sum_{i<j} \frac{1}{r_{ij}} - \sum_{A=1}^N \sum_{i=1}^n \frac{Z_A}{r_{iA}}$$

- **The Born-Oppenheimer** approximation: nuclei are much heavier than electrons, nuclear kinetic energy is zero, inter-nuclear potential energy constant.

- Electronic structure theory

- Electronic Hamiltonian

$$\hat{H}_{\text{elec}} = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 - \sum_{A=1}^N \sum_{i=1}^n \frac{Z_A}{r_{iA}} + \sum_{i<j} \frac{1}{r_{ij}}$$

- only normalized wavefunctions (with Dirac notation)

$$\int d\vec{r}_1 \int d\vec{r}_2 \cdots \int d\vec{r}_n |\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n)|^2 = 1 \quad \langle \Psi | \Psi \rangle = 1$$

Expectation values = observable properties

$$\int d\vec{r}_1 \int d\vec{r}_2 \cdots \int d\vec{r}_n \Psi^*(\dots) \hat{A} \Psi(\dots) \equiv \langle \Psi | \hat{A} | \Psi \rangle$$

- Electronic structure theory

- Foundation of approximate methods is necessary, $N_{\text{at}} \sim 10^{26}$

$$\hat{H}\Psi_0 = E_0\Psi_0$$

- Exact ground state solution:
- Variation theorem
- $E[\Psi]$ is the energy **functional**
- Hartree-Fock (HF) solution when minimizing $E[\Psi_{\text{SD}}]$
- Ψ_{SD} is a Slater determinant

$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle \geq E_0$$

$$\Psi_{\text{SD}} = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \cdots & \psi_n(1) \\ \psi_1(2) & \psi_2(2) & \cdots & \psi_n(2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(n) & \psi_2(n) & \cdots & \psi_n(n) \end{vmatrix}$$

- Describes system as n one-electron systems with an effective potential

Density Functional Theory: background • Electronic structure theory

- HF theory: we need to solve n coupled 1-electron equations

$$\underbrace{\left[-\frac{1}{2}\nabla^2 + v_{\text{nuc}}(\vec{r}) + v_J(\vec{r}) - \hat{K} \right]}_{\hat{f}} \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r})$$

- These are the *Fock equations* and \hat{f} is the Fock operator
- Terms for kinetic energy, nuclear potential, Coulomb and exchange energy

$$v_{\text{nuc}}(\vec{r}_1) = -\sum_A Z_A/r_{1A}$$

$$v_J(\vec{r}_1)\psi(\vec{r}_1) = \sum_i \int d\vec{r}_2 \frac{\psi_i^*(\vec{r}_2)\psi_i(\vec{r}_2)}{r_{12}} \psi(\vec{r}_1)$$

$$\hat{K}\psi(\vec{r}_1) = \sum_i \int d\vec{r}_2 \frac{\psi_i^*(\vec{r}_2)\psi_i(\vec{r}_1)}{r_{12}} \psi(\vec{r}_2)$$

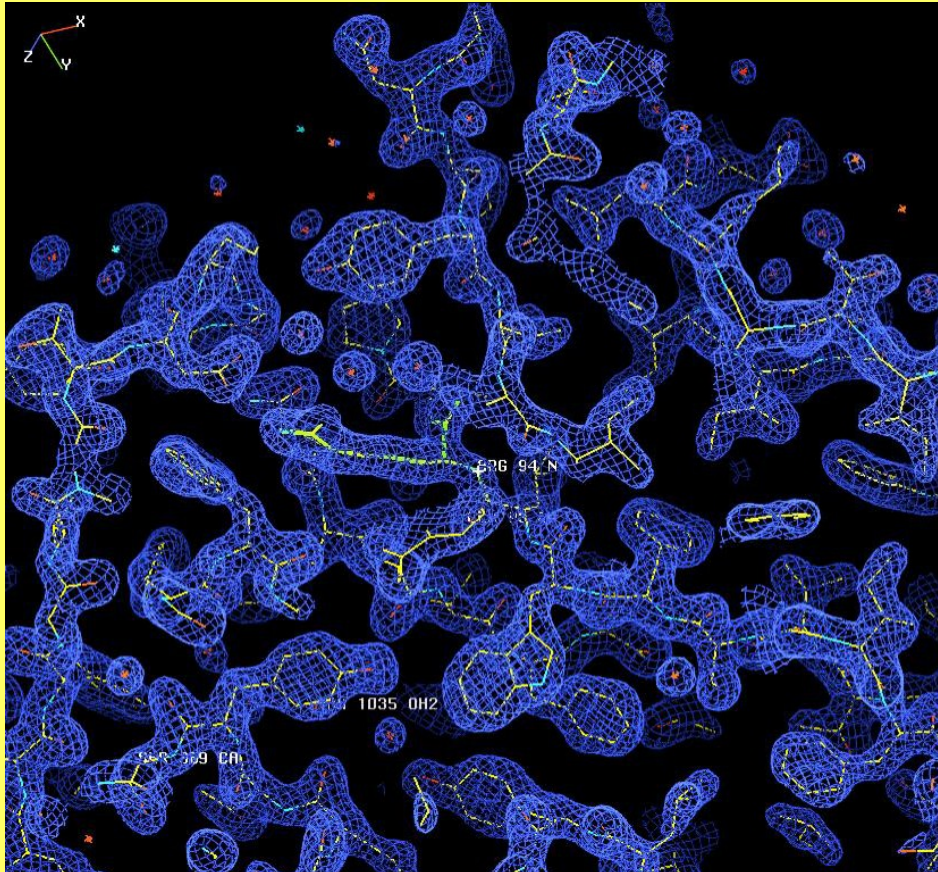
Density Functional Theory: background

• Electronic structure theory

- density - observable in X-ray diffraction experiments
- $\rho(\mathbf{r})d\mathbf{r}$ probability of finding an electron in the volume $d\mathbf{r}$

$$\rho(\vec{r}_1) = n \int d\vec{r}_2 \int d\vec{r}_3 \dots \int d\vec{r}_n |\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n)|^2$$

Electron density is related to the wavefunction



Nuclear interaction energy can be obtained directly

$$\left\langle \Psi \left| -\sum_{iA} \frac{Z_A}{r_{iA}} \right| \Psi \right\rangle = \int d\vec{r} \rho(\vec{r}) v_{\text{nuc}}(\vec{r})$$

$$v_{\text{nuc}}(\vec{r}_1) = -\sum_A \frac{Z_A}{r_{1A}}$$

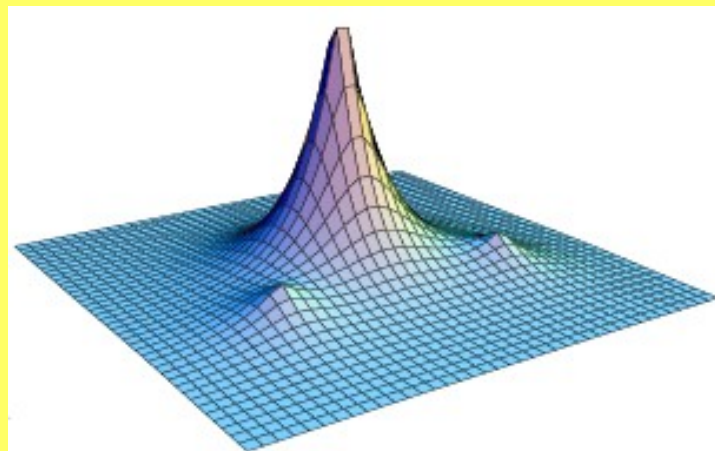
E. Bright Wilson's (1965) interpretation:

- The integral of an exact ground-state density $\rho(\mathbf{r})$ provides n

$$\int d\vec{r} \rho(\vec{r}) = n$$

- Slope of density at the nuclei give charges (cusp condition)
- The density tells us the number of electrons; the positions and charges of the nuclei,
- This is all that is needed to write down H

- The density has peaks coinciding with the nuclei



The Hohenberg-Kohn Theorems, 1965 (I & II)

(I) The density $\rho(\mathbf{r})$ uniquely determines the Hamiltonian

- Integral gives the number of electrons:

$$\int d\vec{r} \rho(\vec{r}) = n$$

- 1) Take the exact ground state density for some system (X-ray, EDX,).
- 2) Use ρ to obtain hamiltonian H .
- 3) Form and solve the Schroedinger equation.
- 4) Obtain the exact ground state energy.

Summary: $E_0 = E[\rho]$

(II) Energy functional of density and can be obtained in **variational way**.

There is a variational **density functional theory**, where :

$$E[\rho] = \int d\vec{r} \rho(\vec{r}) v_{\text{nuc}}(\vec{r}) + F_{\text{HK}}[\rho]$$

$$E[\rho] = F_{\text{HK}}[\rho] + \int d\vec{r} v_{\text{nuc}}(\vec{r})\rho(\vec{r})$$

universal but big and unknown

system-specific, big and known

Kohn-Sham Theory

$$E[\rho] = T[\rho] + V_{\text{ee}}[\rho] + \int d\vec{r} v_{\text{nuc}}(\vec{r})\rho(\vec{r})$$

$$E[\rho] = T[\rho] + \underbrace{J[\rho] + E'_{\text{xc}}[\rho]} + \int d\vec{r} v_{\text{nuc}}(\vec{r})\rho(\vec{r})$$

the biggest unknown term

Coulomb term
big and known

unknown but small

$$T_s = \langle \Psi_{\text{SD}} | \hat{T} | \Psi_{\text{SD}} \rangle - \frac{1}{2} \sum_{i \in \text{occ}} \langle \psi_i | \nabla^2 | \psi_i \rangle$$

$$T[\rho] = T_s + T_c[\rho]$$

Kohn-Sham equations

$$E_{\text{KS}} = T_s + T_c[\rho] + J[\rho] + E'_{\text{xc}}[\rho] + \int d\vec{r} v_{\text{nuc}}(\vec{r})\rho(\vec{r})$$

$$E_{\text{KS}} = T_s + J[\rho] + E_{\text{xc}}[\rho] + \int d\vec{r} v_{\text{nuc}}(\vec{r})\rho(\vec{r})$$

$$E_{\text{xc}}[\rho] = T_c[\rho] + E'_{\text{xc}}[\rho]$$

E_{KS} need to be minimized,
 E_{xc} - approximated

$$v_{\text{xc}} = \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho}$$

exchange-
correlation

• Hartree-Fock equations

$$\left[-\frac{1}{2}\nabla^2 + v + v_J - \hat{K} \right] \psi_i = \epsilon_i \psi_i$$

• Kohn-Sham equations

$$\left[-\frac{1}{2}\nabla^2 + v + v_J + v_{\text{xc}} \right] \psi_i = \epsilon_i \psi_i$$

How to approximate E_{xc} (LDA -local density approximation) ?

$E_{xc}[n]$ is a sum of contributions from each points, depending only upon the density at each point, independent of other points.

$$E_{xc}[n] = \int d^3r n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r})) \quad \epsilon_{xc}(n) \text{ energy exch.-corr. per electron}$$

There are many analytical expressions for E_{xc} :

- Barth-Hedin, Vosko-Nusair, Lunqvist, Perdew-Wang, ... (1970-80),
- Car-Parinello (QMC)

LSD -local spin density approximation (magnetic systems)

GGA -generalised gradient approximation

$$E_{xc}^{GGA}[n^\uparrow, n^\downarrow] = \int d^3r n(\mathbf{r}) \epsilon_{xc}(n^\uparrow, n^\downarrow, \nabla n^\uparrow, \nabla n^\downarrow)$$

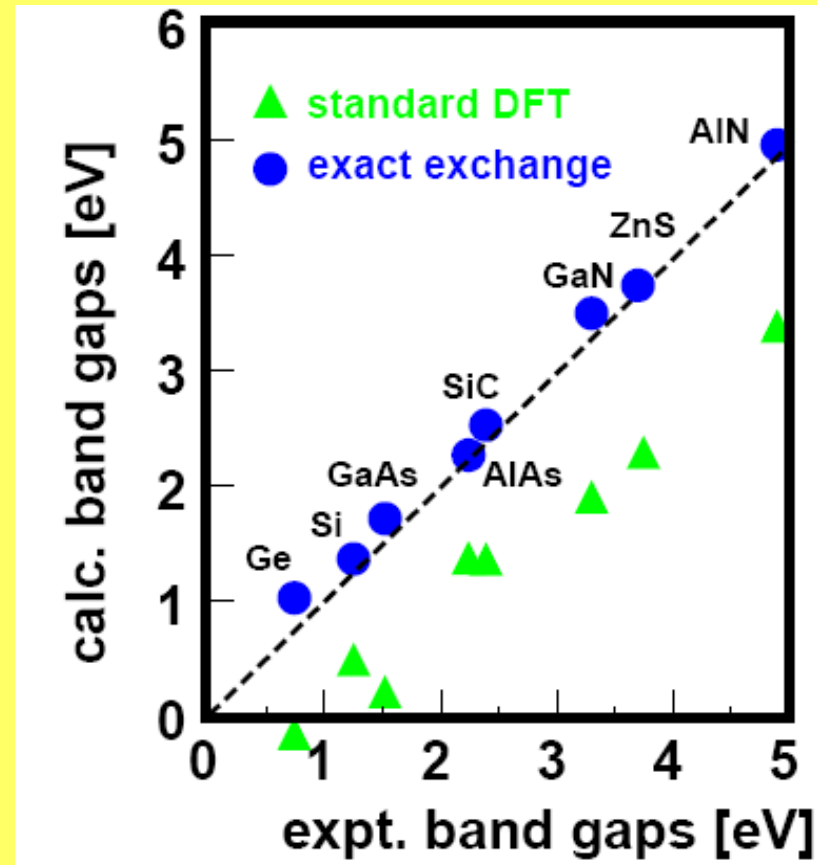
$$\equiv \int d^3r n(\mathbf{r}) \epsilon_x^{hom}(n) F_{xc}(n^\uparrow, n^\downarrow, \nabla n^\uparrow, \nabla n^\downarrow),$$

Summary

- Density functional theory is an exact reformulation of many-body QM in terms of the **probability density** rather than the wave function.

- The ground state energy can be obtained by minimisation of the energy functional $E[n]$. All we know about the functional that it exists, but **its form is unknown**.

- KS reformulation in terms of single-particle orbitals helps to develop of approximations (LDA, GGA, GW,...) and **is used** in current DFT calculations today.



Electronic structure calculations (APW, KKR)

(Linearized) Augmented Plane Waves (LAPW)

$$\phi_{\vec{G}}^{\vec{k}}(\vec{r}, E) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\vec{k}+\vec{G})\vec{r}} & \vec{r} \in I \\ \sum_{lm} A_{lm}^{\alpha, \vec{k}+\vec{G}} u_l^{\alpha}(|\vec{r}-\vec{r}_{\alpha}|, E) Y_{lm}(\hat{r}-\vec{r}_{\alpha}) & \vec{r} \in S_{\alpha} \end{cases}$$

$$u_l^{\alpha}(|\vec{r}-\vec{r}_{\alpha}|, E) = u_l^{\alpha}(|\vec{r}-\vec{r}_{\alpha}|, E_l^{\alpha}) + (E - E_l^{\alpha}) \frac{\partial u_l^{\alpha}}{\partial E} \Big|_{E=E_l^{\alpha}} + o(E - E_{\alpha})^2$$

$$\phi_{\vec{G}}^{\vec{k}}(\vec{r}, E) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\vec{k}+\vec{G})\vec{r}} & \vec{r} \in I \\ \sum_{lm} [A_{lm}^{\alpha, \vec{k}+\vec{G}} u_l^{\alpha}(|\vec{r}-\vec{r}_{\alpha}|, E_l^{\alpha}) + B_{lm}^{\alpha, \vec{k}+\vec{G}} \frac{\partial u_l^{\alpha}}{\partial E} (|\vec{r}-\vec{r}_{\alpha}|, E_l^{\alpha})] Y_{lm}(\hat{r}-\vec{r}_{\alpha}) & \vec{r} \in S_{\alpha} \end{cases}$$

Green function Korringa-Kohn-Rostoker (KKR)

$$G(E) = \sum_{s=(+,-)} \sum_{k=1}^K \int_{V_k} d^3r \langle s, \mathbf{r} + \mathbf{a}_k | G(E) | s, \mathbf{r} + \mathbf{a}_k \rangle.$$

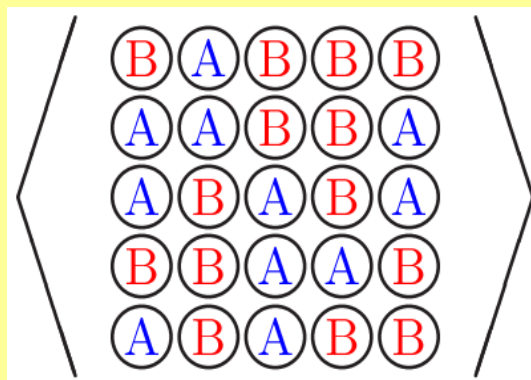
$$N(E) = -\frac{1}{\pi} \text{Im} \int_{-\infty}^E dE' G(E')$$

$$\begin{aligned} \langle s' \mathbf{r}' + \mathbf{a}_{k'} | G(\mathbf{k}E) | s \mathbf{r} + \mathbf{a}_k \rangle &= - \sum_{\sigma L} J_{\sigma L}^{(k)}(s' \mathbf{r}') Z_{\sigma L}^{(k)}(s \mathbf{r}) \delta_{k'k} \\ &+ \sum_{\sigma' L', \sigma L} Z_{\sigma' L'}^{(k')}(s' \mathbf{r}') [\tau^{-1} - \mathbf{B}(\mathbf{k}E)]_{k' \sigma' L', k \sigma L}^{-1} Z_{\sigma L}^{(k)}(s \mathbf{r}). \end{aligned}$$

Linearized Muffin-Tin Orbitals (LMTO); tight-binding (TB)
Pseudopotential Methods

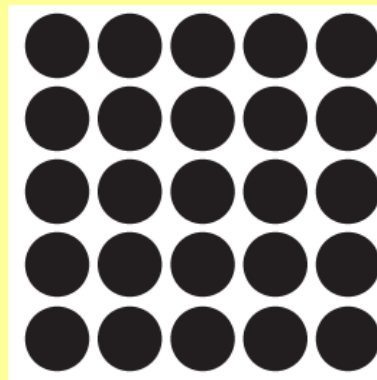
KKR-CPA method & complex bands

- Disordered alloys: ~~periodic~~ - Coherent Potential Approximation (CPA):



CPA “trick”

=



CPA condition

$$c_A T^A + c_B T^B = T^{CP}$$

In multi-atomic systems more imagination needed !

$$T_{k'\sigma'L',k\sigma L}^{CP} = \frac{1}{N} \sum_{\mathbf{k} \in BZ} [\tau_{CP}^{-1} - B(E, \mathbf{k})]_{k'\sigma'L',k\sigma L}^{-1}$$

CPA crystal - restored periodicity

price: complex potential

CPA much better than virtual crystal approx. V_{VCA}

Present KKR-CPA code allows for treatment of more than 2 atoms on disordered site, but within *muffin-tin* potential (problem with CPA condition), CPA is also solved self-consistently; imaginary part of $E(\mathbf{k})$ related to electron life-time due to disorder !

KKR-CPA method for disordered alloys

Korringa-Kohn-Rostoker with coherent potential approximation

$$G(E) = \sum_{s=(+,-)} \sum_{k=1}^K \int_{V_k} d^3r \langle s, \mathbf{r} + \mathbf{a}_k | G(E) | s, \mathbf{r} + \mathbf{a}_k \rangle.$$

Bansil, Kaprzyk, Mijnaerends, (JT),
Phys. Rev. B (1999) **conventional KKR**

Full GF

Stopa, Kaprzyk, (JT),
J.Phys.CM (2004)
novel formulation of KKR

$$\begin{aligned} & \langle s', \mathbf{r}' + \mathbf{a}_{k_{CP}} | G^{A(B)}(E) | s, \mathbf{r} + \mathbf{a}_{k_{CP}} \rangle \\ &= - \sum_{\sigma L} J_{\sigma L}^{A(B)}(s', \mathbf{r}') Z_{\sigma L}^{A(B)}(s\mathbf{r}) \\ &+ \sum_{\sigma' L', \sigma L} Z_{\sigma' L'}^{A(B)}(s', \mathbf{r}') T_{k_{CP} \sigma' L', k_{CP} \sigma L}^{A(B)} Z_{\sigma L}^{A(B)}(s\mathbf{r}) \end{aligned}$$

$$\begin{aligned} & \langle s', \mathbf{r}' + \mathbf{a}_{k'} | G(E) | s, \mathbf{r} + \mathbf{a}_k \rangle \\ &= - \sum_{\sigma L} J_{\sigma L}^{(k)}(s', \mathbf{r}') Z_{\sigma L}^{(k)}(s\mathbf{r}) \delta_{kk'} \\ &+ \sum_{\sigma' L', \sigma L} Z_{\sigma' L'}^{(k')} (s', \mathbf{r}') T_{k' \sigma' L', k \sigma L}^{CP} Z_{\sigma L}^{(k)}(s\mathbf{r}) \end{aligned}$$

$$\begin{aligned} G(E) = & - \frac{d}{dE} \left\{ \frac{1}{N} \sum_{\mathbf{k} \in BZ} \text{Tr} \ln [G_0^{-1}(E, \mathbf{k}) + D^{(j)} - D_{CP}]^{-1} \right\} \\ & - \frac{d}{dE} \{ c_A \text{Tr} \ln [\Psi_A^{-1} G^A] + c_B \text{Tr} \ln [\Psi_B^{-1} G^B] \\ & - \text{Tr} \ln G^{CP} \} + \frac{d}{dE} \left\{ \sum_{k \neq k_{CP}} \text{Tr} \ln [\Psi^{(k)}] \right\}, \quad (2.22) \end{aligned}$$

$$T_{k' \sigma' L', k \sigma L}^{CP} = \frac{1}{N} \sum_{\mathbf{k} \in BZ} [\tau_{CP}^{-1} - B(E, \mathbf{k})]_{k' \sigma' L', k \sigma L}^{-1}$$

CPA $c_A T^A + c_B T^B = T^{CP}$

Density of states $N(E) = - \frac{1}{\pi} \text{Im} \int_{-\infty}^E dE G(E)$

Lloyd formula *Kaprzyk et al. Phys. Rev. B (1990)*

Fermi energy $N(E_F) = Z$

Ground state properties

KKR-CPA code (S. Kaprzyk, Krakow)

Total density of states DOS

$$N(E) = -\frac{1}{\pi} \text{Im} \int_{-\infty}^E dE G(E)$$

Component, partial DOS

$$\rho_{\sigma}(E) = \frac{\partial}{\partial E} N_{\sigma}(E).$$

Total magnetic moment

$$\mu = N_{+}(E_F) - N_{-}(E_F)$$

Spin and charge densities

$$\rho_{\sigma}^{(k)}(\mathbf{r}) = -\frac{1}{\pi} \int_{-\infty}^{E_F} dE \langle \sigma, \mathbf{r} + \mathbf{a}_k | G(E) | \sigma, \mathbf{r} + \mathbf{a}_k \rangle$$

Local magnetic moments

$$\mu^{(k)} = \mu_B \int_{\Omega_k} d^3r S^{(k)}(\mathbf{r})$$

Fermi contact hyperfine field

$$H_{Fermi} = \frac{8}{3} \pi \mu_B [\rho_{\uparrow}(0) - \rho_{\downarrow}(0)].$$

Bands $E(\mathbf{k})$, total energy, electron-phonon coupling, magnetic structures, transport properties, magnetocaloric, photoemission spectra, Compton profiles, superconductivity, ...