Electronic Structure of Correlated systems

2019 Questaal Hands-On Course

	Monday	***Tuesday***	***Wednesday***	***Thursday***	***Friday***
08:15	***coach to DL***	***coach to DL***	***coach to DL***		***coach to DL***
08:45-09:00	***registration***				
09:00-10:30	Introduction to LMTO and Electronic Structure: Mark van Schilfgaarde	Talk: Myrta Grüning (Queen's University Belfast)	Talk: Christoph Friedrich (Jülich) *coffee break 10:00*	***coach to DL 09:15***	Installation & Trouble Shooting (DP)
10:30-11:00	*coffee break*	*coffee break*	*qsGW: student's topics*	LMTO topics: ASA and GF (MvS, JJ, DP)	*coffee break*
11:00-12:30	DFT with LMF (JJ)	Talk: Introduction to qsGW (MvS)	Talk: Brian Cunningham (Queen's University Belfast)	*coffee break 11:00* Talk: Dynamical Mean Field Theory (Swagata Acharya)	*qsGW: student's topics*
12:30-13:30	*lunch*	*lunch*	*lunch*	*lunch*	*lunch*
13:30-14:30	Talk: Laurent Chapon (Diamond Light Source)	qsGW (MvS)	BSE (BC)	qsGW+DMFT (SA, FJ)	*Q&A*
14:30-15:00	*coffee break*	*coffee break*	*coffee break*		
15:00-16:30	Properties with LMF (MvS,JJ,DP)	qsGW (MvS)	BSE (BC)	*coffee break 15:00* qsGW+DMFT (SA, FJ)	*coffee break* *ends*
16:30-18:00	LDA+U, SO (JJ)	*qsGW: student's topics*	Talk: Phonon Self Energy (Savio Laricchia) *qsGW: student's topics*		
18:00	***coach to Chester***	***coach to Chester***		***coach to Chester***	

Leon Petit and Jerome Jackson: Workshop organisers

Dmitar Pashov: manages Questaal

Many-electron systems

The Hamiltonian (lower case i,j ⇒ e^-; upper case I,J ⇒ N^+)

$$H = T_{\text{el}} + T_{\text{nuc}} + V_{\text{el-el}} + V_{\text{el-nuc}} + V_{\text{nuc-nuc}}$$

$$H = \sum_i \frac{p_i^2}{2m_i} + \sum_I \frac{P_I^2}{2M_I} + \underset{\substack{\uparrow \\ e^- e^-}}{\sum_{i>j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}} + \underset{\substack{\uparrow \\ e^- N^+}}{\sum_{iI} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|}} + \underset{\substack{\uparrow \\ N^+ N^+}}{\sum_{I>J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}}$$

- Forces: electrostatic interactions between charged particles. Mostly dominant for chemistry and solid state physics
- All that enters are nuclear positions R_I, nuclear and electron masses M_I and m_i, and nuclear charges Z_I.
- *One equation* predicts extremely rich and diverse phenomena: transport, mechanical strength, superconductivity, and ⋯ choose your favorite!

Range of observables

All physical observables are calculable (in principle) as expectation values of the (many-body) wave function.

Ground state (from $E = \langle H \rangle$)

- heats of formation
- elastic constants, phonon spectra
- structure
- defect formation energies and diffusion barriers, catalysis
- magnetic structure
- Piezoelectricity

Excited State

- Energy bands
- Conductivity, dielectric response
- Optical absorption, emission
- Magnetic excitations
- Almost any spectroscopy, e.g. EELS, photoemission

But ⋯ also very difficult to solve! Especially when correlations are strong

Many-body Hamiltonian doesn't factor

The problem remains: solve the SE for this hamiltonian!

Huge problem ← V_{int} **involves pairs of electrons**

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i,I}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} - \sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$$

Almost every description we have is based on the independent particle picture: even special cases (Cooper pairs) are "particles".

But V_{int} precludes factorization of the many-body Ψ e.g.:

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) \rightarrow \psi_1(\mathbf{r}_1) \times \psi_2(\mathbf{r}_2) \times \ldots \times \psi_N(\mathbf{r}_N)$$

Without it, we can't even talk about the particles as though they are independent --- just a "soup"

Worse: V_{int} is both large (e^2=14.4 eV-A) and has infinite range. Electrons interact strongly with each other. Not clear can we can sensibly talk about independent particles at all ..

Fortunately, for most part, Nature is kinder than that.

Quasiparticles

- How to cast many-body problem into a collection of independent particles ?

$$\Psi\,(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) \rightarrow \psi_1(\mathbf{r}_1) \times \psi_2(\mathbf{r}_2) \times \ldots \times \psi_N(\mathbf{r}_N)$$

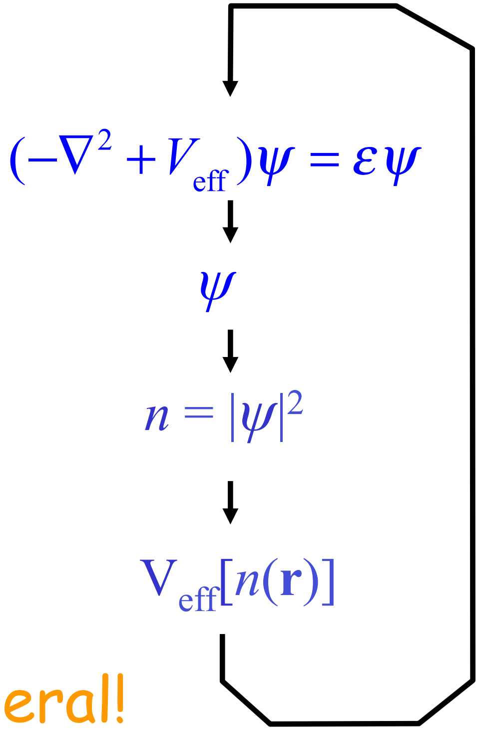
- Resolution: each e^- contributes some effective external field to the entire system.
- All e^- move in the presence of the collective effective field.
- Quasiparticles (Landau): a "particle," e.g. electron, really consists of a normal ("bare") electron + cloud of other "stuff."
- Quasiparticles behave as though they are nearly independent of each other. Residual interactions (difference betw/ effective field and actual field) ⇒ quasiparticles decay after finite time. Lifetime cannot be too short if QP picture is to be meaningful.

- Q: How to formulate a theory for the effective field?

Aside: Self-consistency

For the moment, let's assume we have some method in hand to construct $V^{\mathrm{eff}}(\mathbf{r})$. Assume $V^{\mathrm{eff}}(\mathbf{r})$ generated from $n(\mathbf{r})$ for simplicity.

Chicken-and egg problem: The density $n(\mathbf{r})$ generates $V^{\mathrm{eff}}(\mathbf{r})$, while $V^{\mathrm{eff}}(\mathbf{r})$ generates $n(\mathbf{r})$ through $V^{\mathrm{eff}}(\mathbf{r}) \to \psi(\mathbf{r}) \to n(\mathbf{r})$.
Need one to get the other



$$(-\nabla^2 + V_{\mathrm{eff}})\psi = \varepsilon\psi$$

$$\psi$$

$$n = |\psi|^2$$

$$\mathrm{V}_{\mathrm{eff}}[n(\mathbf{r})]$$

Resolution: *guess* a trial $V^{\mathrm{eff}}(\mathbf{r})$, and iterate until the V^{eff} that *generates* ψ is the same as the V^{eff} *generated by* ψ.

Self-consistency places a central role for any approximate method. A nontrivial issue in general!

Simplest formulation of V^{eff} : Hartree Fock

How to formulate the noninteracting reference system?

Hartree-Fock was the first. Write the hamiltonian this way:

$$H=\sum_i h_0(\mathbf{x}_i)+\frac{1}{2}\sum_{i\neq j} v(\mathbf{x}_i,\mathbf{x}_j)+V_{\text{nuc}},\qquad \mathbf{x}=(\mathbf{r},\xi)$$

Space + spin

$$h_0(\mathbf{x}_i)=-\frac{\nabla_i^2}{2m_i}-\sum_I v(\mathbf{x}_i,\mathbf{R}_I),\qquad v(\mathbf{x}_i,\mathbf{x}_j)=\frac{e^2}{\left|\mathbf{r}_i-\mathbf{r}_j\right|}$$

Define a (complete) set of one-particle orbitals $\psi_i(\mathbf{x})$.

Make a Slater Determinant of N them: $\left|\Psi\right\rangle = N^{-1/2}\det|\psi_i(\mathbf{x}_k)|$

Variational principle: vary the shape $\psi_i(\mathbf{x})$ until E is minimum

$$\delta\left\langle\Psi\right|H\left|\Psi\right\rangle=0 \quad \text{subject to constraints} \quad \int\psi_i^*(\mathbf{x})\psi_j(\mathbf{x})d\mathbf{x}=\delta_{ij}$$

One Electron Hamiltonian

$\delta\langle\Psi|H|\Psi\rangle/\delta\psi_i = 0$ generates effective one-body H_0:

$$(h + V_H + V_{\mathrm{x}})\psi_k = \varepsilon_k \psi_k$$

↑

nonlocal operator

$$V_{\mathrm{x}}\psi_k = \int V_{\mathrm{x}}(\mathbf{x},\mathbf{x}')\psi_k(\mathbf{x}')d\mathbf{x}'$$

$$V_H(\mathbf{x}) = \int v(\mathbf{x},\mathbf{x}')\rho(\mathbf{x}')d\mathbf{x}'$$

Hartree

$$V_{\mathrm{x}}(\mathbf{x},\mathbf{x}') = -v(\mathbf{x},\mathbf{x}')\rho(\mathbf{x},\mathbf{x}')$$

Exchange

density

$$\rho(\mathbf{x}) = \sum_{i=1}^{N}\psi_i^*(\mathbf{x})\psi_i(\mathbf{x})$$

density matrix

$$\rho(\mathbf{x},\mathbf{x}') = \sum_{i=1}^{N}\psi_i^*(\mathbf{x})\psi_i(\mathbf{x}')$$

Ground state: only the lowest N states are filled; only the first N are ψ_i, ε_i are needed.

Koopman’s theorem: the ε_i correspond to excitation energies

$$E[N] - E[N-1, i \text{ empty}] = \varepsilon_i$$

(assumes the ψ_i does not relax after the particle is excited)

Features of the Hartree-Fock Approximation

- Build Ψ from Slater determinants of 1-particle ψ_1, ψ_2, …
  - e.g for two particles: $\Psi(\mathbf{r}_1,\mathbf{r}_2) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) - \psi_2(\mathbf{r}_1)\psi_1(\mathbf{r}_2)$
  - Satisfies self-interaction and symmetry (exclusion principle)
  - Slater Determinant ⇒ limited correlation : For example, $\Psi(\mathbf{r}_1,\mathbf{r}_2) = 0$ when $\mathbf{r}_1 = \mathbf{r}_2$. (called "exchange")
  - Potential is now "Hartree" (e.s.) + "Exchange" Exchange is very important: explains origin of magnetism as a consequence of the Pauli Exclusion principle.
- Simplest ab initio theory consistent with QM.
  - What is put in is well defined.
  - Effective potential V^{eff} is real and ω-independent ⇒ effective hamiltonian is a noninteracting, 1-body H_0 .
  - Hamiltonian is nonlocal : $V^{\mathrm{eff}} = V_H + V^{\mathrm{x}}(\mathbf{x},\mathbf{x}')$ ⇒ each e^- sees own V.
  - Correlation underestimated: energy > exact result

Problems with the Hartree-Fock Approximation

- Moderate errors in small molecules (used in chemistry)
- Severe errors in condensed matter
  - Total energy: Fe is predicted to be AFM insulator
Magnetic moment in the FM state is much too large
  - velocity has pathological divergence at E_F in metals

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} + \frac{e^2 k_F}{\pi} f(k/k_F) \quad \text{where } f(x) = -\left[1 + \frac{1-x^2}{2x}\ln\left|\frac{1+x}{1-x}\right|\right], \quad x = \frac{k}{k_F}$$

  - Bandgaps, bandwidths much too large: 5 eV in Si, expt = 1.1 eV
- Largest source of error : v needs to be screened!
- Even simple screening, e.g. Thomas Fermi $v(q) = 1/(q^2 + q^2_{\mathrm{TF}})$ helps a lot. It removes divergence of v_F in metals, reduces bandwidths, magnetic moments …

$$v(r) = 1/r$$

$$v(q) = 1/q^2$$

Choices of the basic variable

Much freedom in how V^{eff} is constructed. Usually V^{eff} made from (or for) a Slater determinant of independent-particle $\psi_i(\mathbf{r})$

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) \rightarrow \psi_1(\mathbf{r}_1) \times \psi_2(\mathbf{r}_2) \times \ldots \times \psi_N(\mathbf{r}_N)$$

Hartree Fock theory is the simplest formally. Assumes a Slater determinant Φ for $\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$. V_i^{eff} is determined from

$$V_i^{\mathrm{eff}}(\mathbf{r}) = \delta\left\langle\Phi\middle|\hat{H}\middle|\Phi\right\rangle / \delta\psi_i(\mathbf{r})$$

Thus the $\psi_i(\mathbf{r})$ are the fundamental variable. Depends on i !

Density functional theory : Fundamental variable is density $n(\mathbf{r})$.
V^{eff} derives from a functional derivative $\delta V/\delta n$,
⇒ every $\psi_i(\mathbf{r})$ feels same V^{eff} much simpler!
Called "locality" … both a blessing and a curse.

Greens' function methods use $G(\mathbf{r},\mathbf{r}',\omega)$ as fundamental variable.
"Goldilocks" approach --- less info than ψ_i but more than $n(\mathbf{r})$.
Intermediate in complexity --- gradually supplanting DFT.

Density Functional Theory : Materials Workhorse

- Hartree-Fock theory was the first to provide realistic solutions to Schrodinger's equation … but
  - Computation is CPU-intensive (scales as N^4)
  - Missing electron correlation is not small!

- In the 1950's Slater developed an efficient way to estimate the Fock exchange. From Hartree Fock V_x was known to vary as $n^{1/3}$ in the homogeneous electron gas.
  Slater's idea: replace the true V_x by a function $V_x(\mathbf{r}) \propto n^{1/3}(\mathbf{r})$. Slater called it the "X-alpha method."

- During the 1960s Slater's idea evolved into a formal theory by Walter Kohn (Nobel laureate in chemistry, 1998).

Density-Functional Theory I

Hohnberg and Kohn (1964) proved that the total energy E can be determined solely from the density. The total energy is written:

$$E_{HK}[n] = T_s[n] + \underbrace{\int d^3r\, n(\mathbf{r}) V_{ext}(\mathbf{r}) + \int d^3r\, n(\mathbf{r}) V_H(\mathbf{r})}_{\textbf{Classical Electrostatics}} + \underbrace{E_{xc}[n]}_{\textbf{Correlations}}$$

- $E=E[n(\mathbf{r})]$ where the density $n(\mathbf{r})$ is the basic variable.
- DFT uses n alone rather than $E=E[\{\psi_i\}]$ as in Hartree-Fock.
  - A “deep” result: n can determine the many-body $\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$
- Formally exact but $E[n]$ is unknown! *Must be* highly nonanalytic
- Particularly pathological is the K.E. functional $T[n]$.
- Hard to see how any universal functional of n can reproduce, e.g. core states of an atom ⇒ discontinuities.
- Similar problems as change occupation of 1-electron levels.
- Tradeoff: $E[n]$ has vastly fewer degrees of freedom than $E[\{\psi_i\}]$ ⇒ complication pushed onto unknown $E_{xc}[n(\mathbf{r})]$.

Density-Functional Theory II : the LDA

A tractable theory: Kohn-Sham ansatz + the Local Density Approx.

1. Assume $T[n]$ is identical to T for a non-interacting system with orbitals constructed from the theory (general to DFT methods)
2. Approximate E_{xc} has some analytic form, calculated e.g. for a reference system such as the homogeneous electron gas

E_{KS} = kinetic + potential energy:

$$E_{KS} = T_s[n] + E_{\text{pot}}[n],$$

$$E_{\text{pot}}[n] = \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + E_H[n] + E_{xc}[n]$$

Use noninteracting ansatz to get at T_{KS} through a back door.

$$H_{KS}^{\text{eff}} \psi_i = -\frac{1}{2}\nabla^2 \psi_i + V^{\text{eff}}(\mathbf{r})\psi_i = \varepsilon_i \psi_i, \qquad V^{\text{eff}}(\mathbf{r}) = \frac{\delta E_{\text{pot}}[n(\mathbf{r})]}{\delta n}$$

$$\left\langle \psi_i \right| -\frac{1}{2}\nabla^2 + V^{\text{eff}} \left| \psi_i \right\rangle = \left\langle \psi_i \,|\, \varepsilon_i \,|\, \psi_i \right\rangle = \varepsilon_i$$

$$T_{KS} = \sum_i \varepsilon_i - \int d\mathbf{r} V^{\text{eff}}(\mathbf{r}) \sum_i \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) = E_{bs} - \int d\mathbf{r} V^{\text{in}}(\mathbf{r}) n^{\text{out}}(\mathbf{r})$$

Properties of the Local Density Approximation

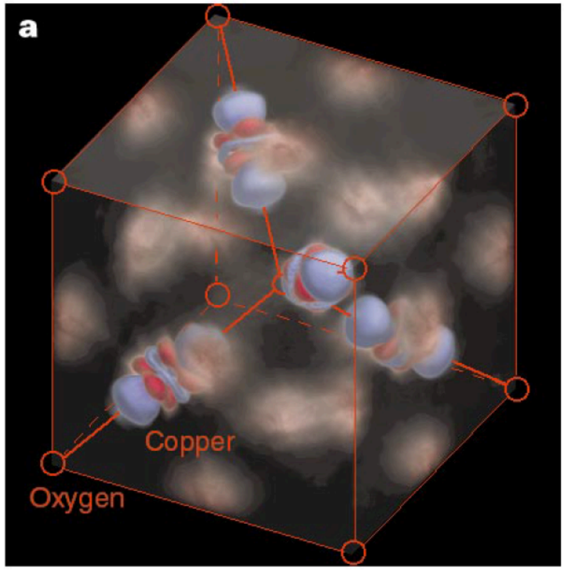
We do not know $E_{\rm xc}[n]$, but must make approximations for it. DFT is very effective because $E_{\rm xc}[n]$ is much less pathological than $T[n]$. Simple approximations (e.g. $E_{\rm xc}[n]$ for the homogeneous electron gas) can give very good results (especially for ground-state properties in weakly correlated systems)

$$E_{\rm xc} \approx \int n(\mathbf{r})\varepsilon_{xc}\left[n(\mathbf{r})\right]d^3\mathbf{r}, \qquad V_{\rm xc}(\mathbf{r}) = \frac{\delta}{\delta n(\mathbf{r})}\left(n(\mathbf{r})\varepsilon_{xc}\left[n(\mathbf{r})\right]\right)$$

Universal ⇒ calculate almost exactly for model, e.g. jellium

- LDA, variants have become standard "workhorse" --- now widely used in almost every branch of science, engineering
- An extremely simple and universal theory … all the complexity is folded into a simple and universal functional.
- Key point: all electrons see same effective potential $V^{\rm eff}(\mathbf{r})$. In contrast to Hartree-Fock (nonlocal $V_{\rm x}(\mathbf{r},\mathbf{r}')$ ⇒ each electron sees a different $V^{\rm eff}(\mathbf{r})$).

Measurements of the electron density



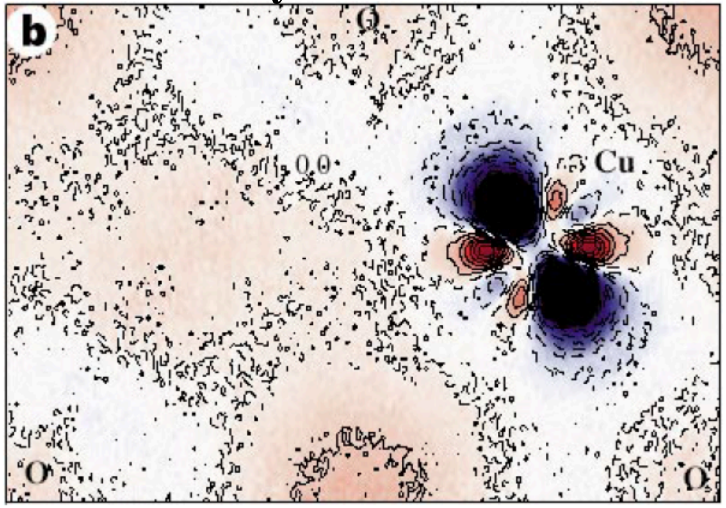
Direct observation of *d*-orbital holes and Cu–Cu bonding in Cu_2O

J. M. Zuo*, M. Kim*, M. O'Keeffe† & J. C. H. Spence*

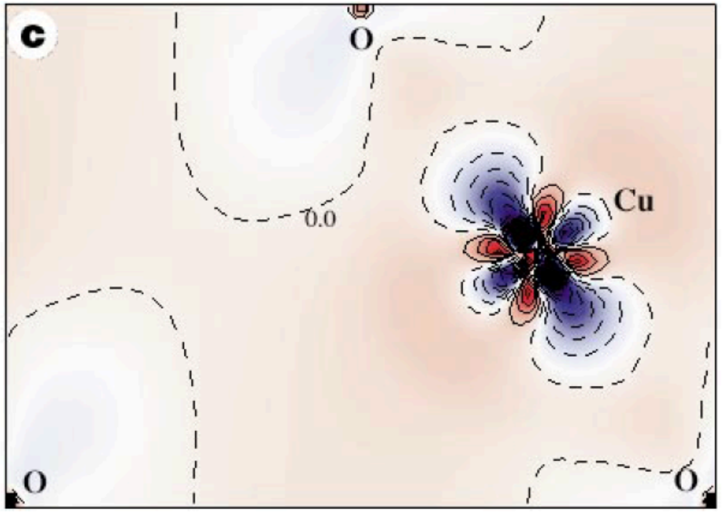
Nature, 401, 49-52 (1999)

DFT is formally exact and can predict any materials property in principle …

X-ray diffraction

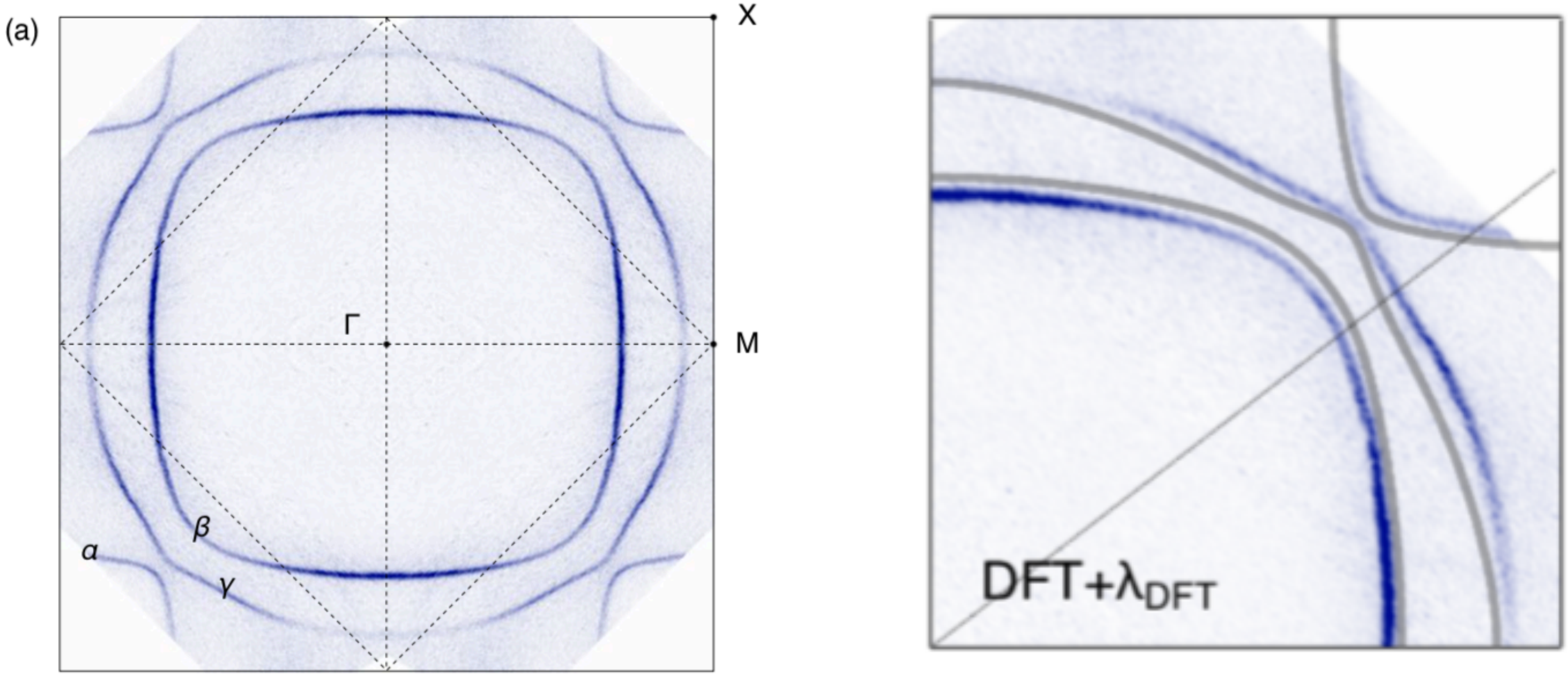


DFT result



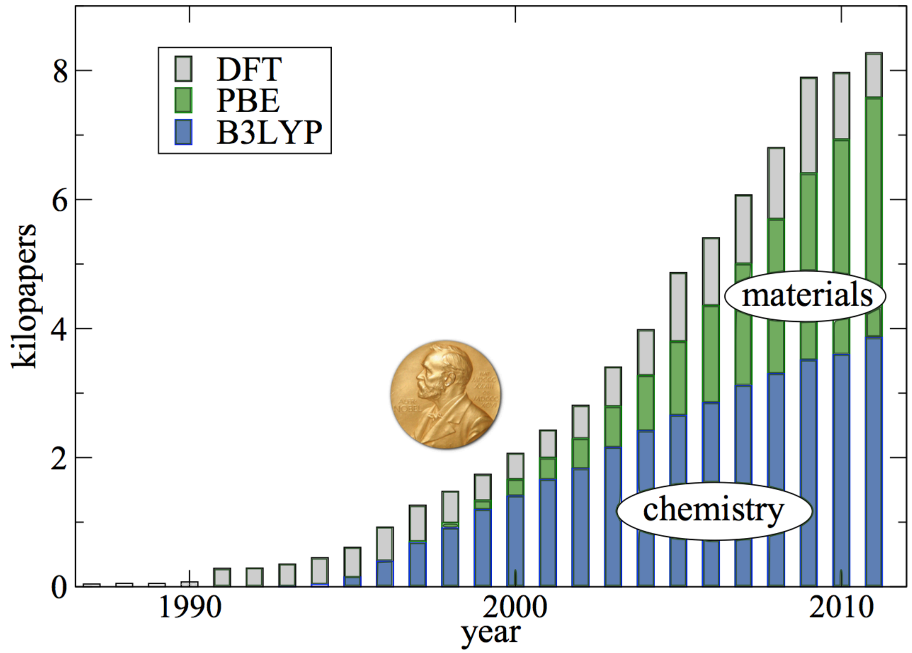
DFT has been tremendously successful!

DFT can work in places where you might not expect it to!



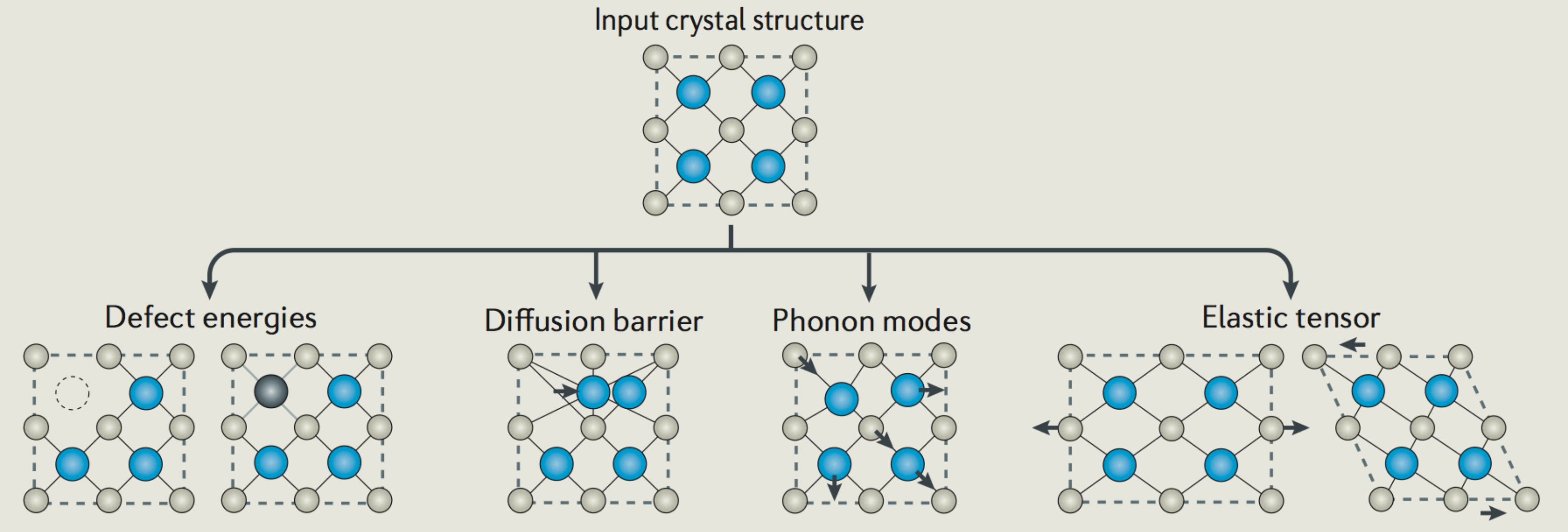
Fermi surface of Sr_2RuO_4 (strongly correlated superconductor) compares nicely to high-quality laser ARPES to DFT.
From A. Tamai et al, arXiv 1812.06531 (2018)

Trajectory of DFT



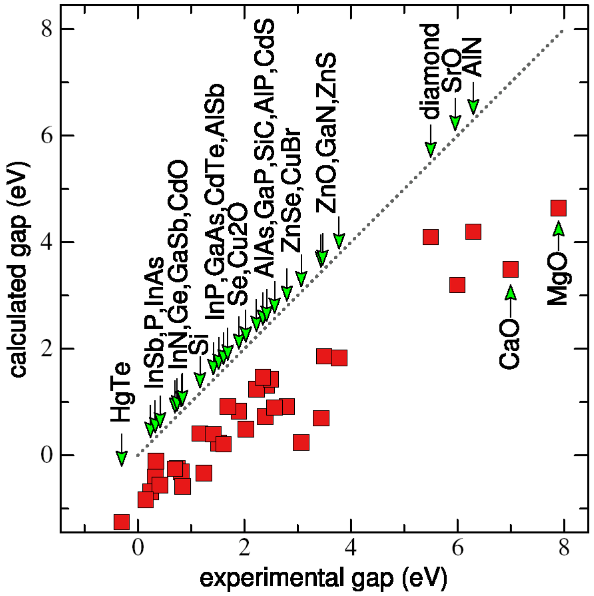
DFT has revolutionized our ability to realistically describe materials properties

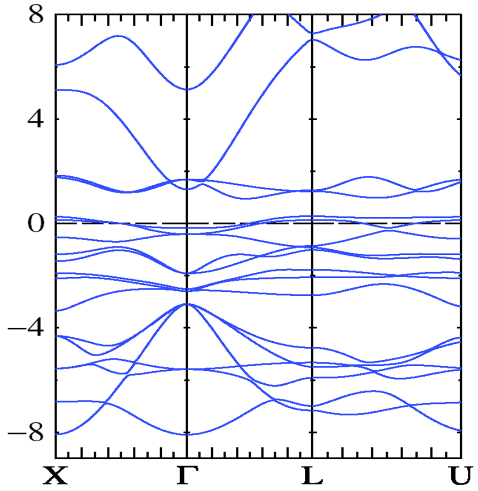
Works best for ground state properties, ie derived from E



Problems with the Local Density Approximation

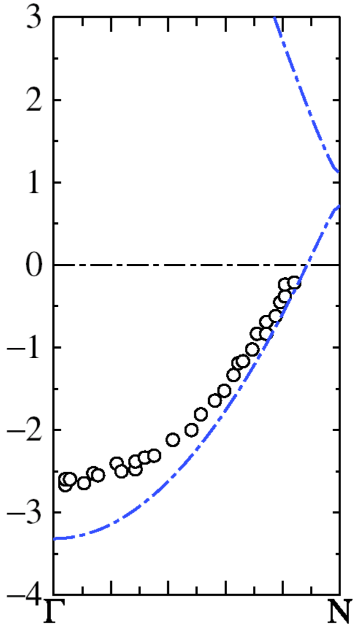
Semi. bandgaps too small

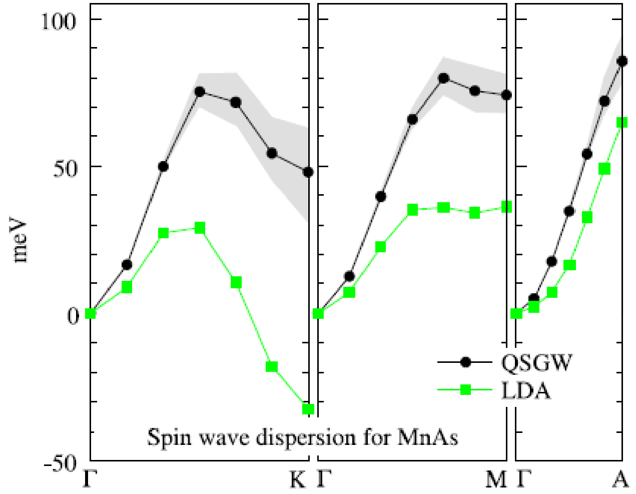




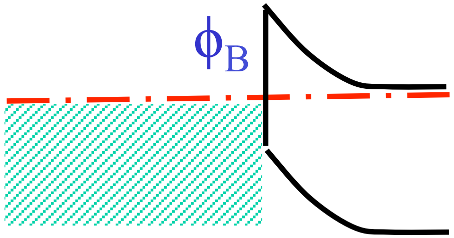
LDA CoO is metalllic but real CoO is AFM insulator w/~2.9 eV gap

Poor Na bands





Magnetism often poorly described



Schottky barriers at metal-semi contacts fall too close to Valence Band

Two possible explanations for LDA error

What is the dominant source of difficulty in the L(S)DA?

Explanation I: Ansatz for $E_{xc}[n]$ is not good enough.

Explanation II: Kohn-Sham ψ_i and eigenvalues ε_i the Lagrange multipliers of the KS hamiltonian

$$\hat{H}^{\sigma}_{KS} = -\frac{\hbar^2}{2m}\nabla^2 + [V^{\sigma}_{KS}(\mathbf{r}) = V_H(\mathbf{r}) + V_{ext}(\mathbf{r}) + V^{\sigma}_{xc}(\mathbf{r})]$$

are fictitious.

Q: How do we assess the source of error?

A: Density-functionalize nonlocal functionals and check.

Not a strict division (there is an interplay between them).
But roughly:

For ground state properties, I is often the primary problem

For excited state properties II is often the primary problem.

Connection between DFT and QP levels

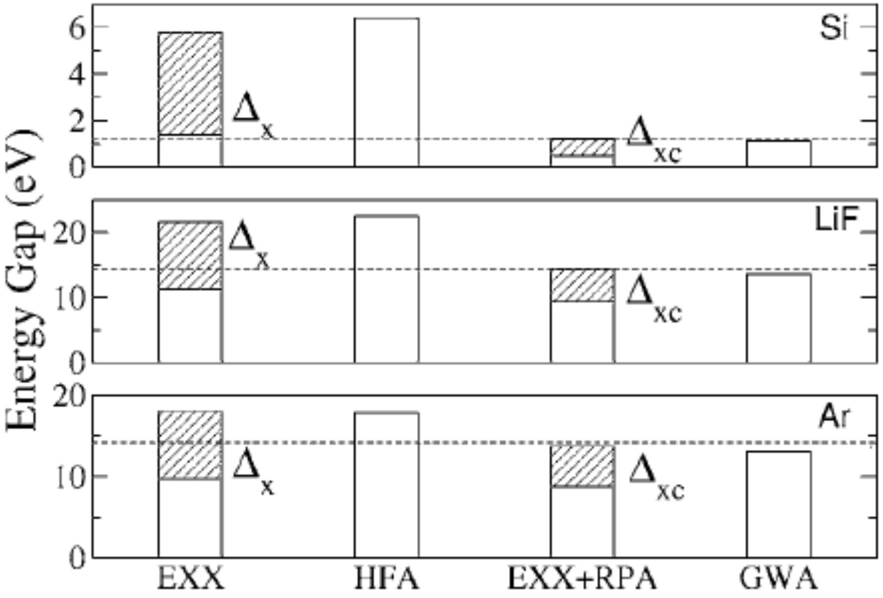
ψ_i and ε_i fictitious ⇒ discontinuity Δ_{xc} in XC potential betw/ highest occupied and lowes unoccupied state

Grüning, Marini, Rubio, (J. Chem. Phys. 124, 154108) evaluated Δ_{xc} by "density-functionalizing" GW (OEP) for Si, LiF,Ar

$$\Delta_{\mathrm{xc}} = \langle \psi_{N+1} | \Sigma_{\mathrm{xc}}^{GW}(\varepsilon_{N+1}) - v_{\mathrm{xc}} | \psi_{N+1} \rangle - \langle \psi_N | \Sigma_{\mathrm{xc}}^{GW}(\varepsilon_N) - v_{\mathrm{xc}} | \psi_N \rangle .$$

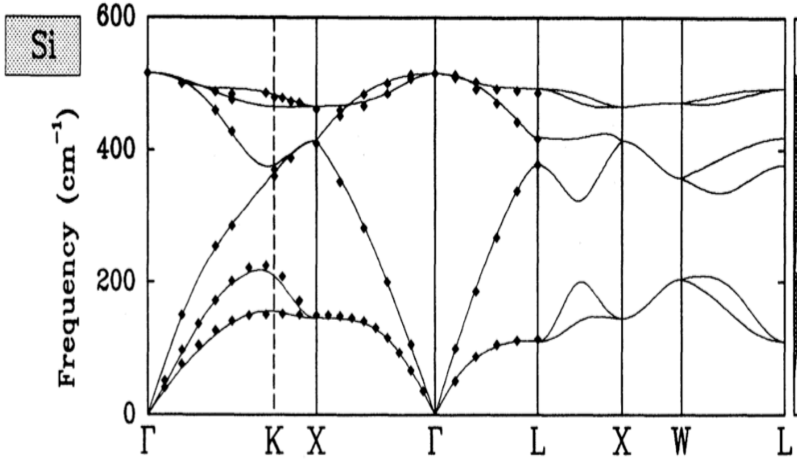
Results show:

OEP gap (EXX+RPA) close to usual LDA gap. Implies Explanation II: the fictitious nature of ψ_i and ε_i are the primary problem

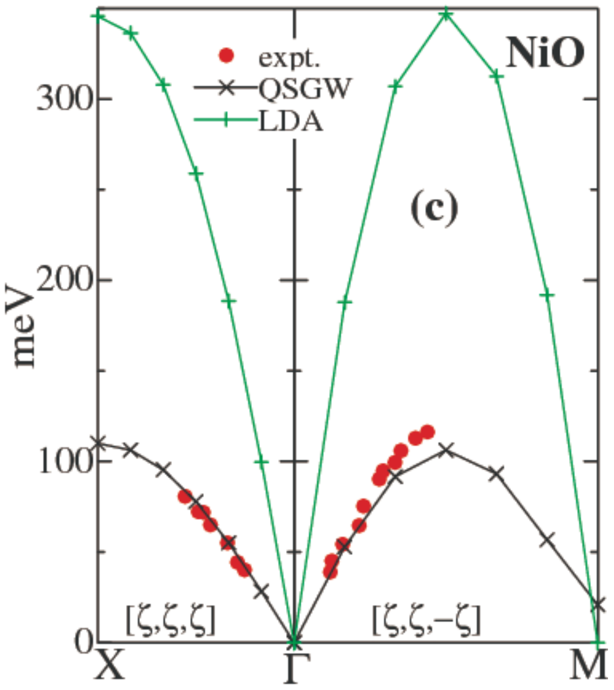


Many attempts to extend, improve on the LDA

- Good ground-state properties in weakly correlated systems.
- Excited state properties are much worse.



Phonon band structure of Si



Spin waves of NiO

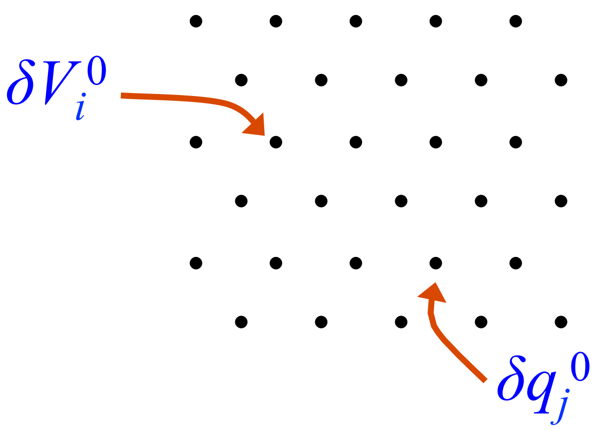
Many attempts to extend LDA. Many significant successes, but improve one or another property in some special cases.

- Removing locality is essential … but LDA starts with an ill-defined ansatz. Without removing it, hard to *systematically* improve on the basic framework

Screening the Coulomb interaction

The coulomb interaction is large and long range. In many-particle systems it is strongly renormalized by screening --- this is the essential difference between Hartree-Fock and GW.

Consider a lattice of points i , with the e$^-$ density initially in equilibrium, perturbed by external potential $\delta\phi_i = \delta V_i^0$ at site i. Supposing the screening charge did not interact with itself---let δq_j^0 be the noninteracting screening charge at j.



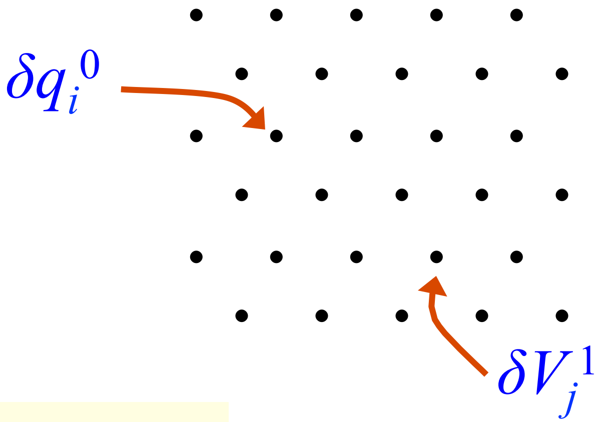
They are connected by the noninteracting response function P^0

$$\delta q_k^0 = P_{kj}^0\,\delta\phi_j$$

← P^0 is called the "irreducible polarizability"

Screening the Coulomb interaction II

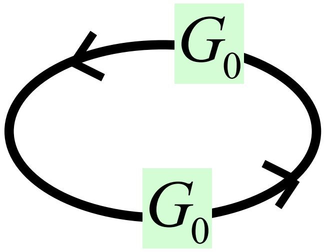
δq_j^0 is determined by change
Green's function $\delta G = G - G^0$
δG comes from Dyson's equation.
Linearize Dyson's equation
$\delta G = G^0 \delta\phi_i G \approx G^0 \delta\phi_i G^0$ to get P^0



$$\delta q_k^0 = \frac{1}{\pi}\mathrm{Im}\int_{-\infty}^{E_F} dz\,\delta G_{kk} = \left[\frac{1}{\pi}\mathrm{Im}\sum_k \int_{-\infty}^{E_F} dz\, G_{kj}^0\, G_{jk}^0\right]\delta\phi_j \equiv P_{kj}^0\,\delta\phi_j$$

Write as $\boxed{P_{kj}^0 = G_{kj}^0\, G_{jk}^0}$

As a Feynman diagram, it is a bubble



Now δq_i^0 generates an electrostatic potential δV_j^1

$$\delta V_j^1 = \sum_i v_{jk}\delta q_i^0$$

δV_i^1 adds to δV_j^0 which induces δq_i^1 ...

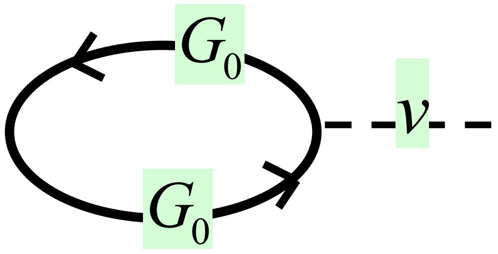
The screening charge in the RPA

The independent particle picture (AKA the RPA or time-dependent Hartree approximation) assumes that the screening only interacts with it self via the classical coulomb interaction.

Then δq_j^0 would induce a potential $\delta V_j^1 = \sum_i v_{ji} \delta q_i^0$

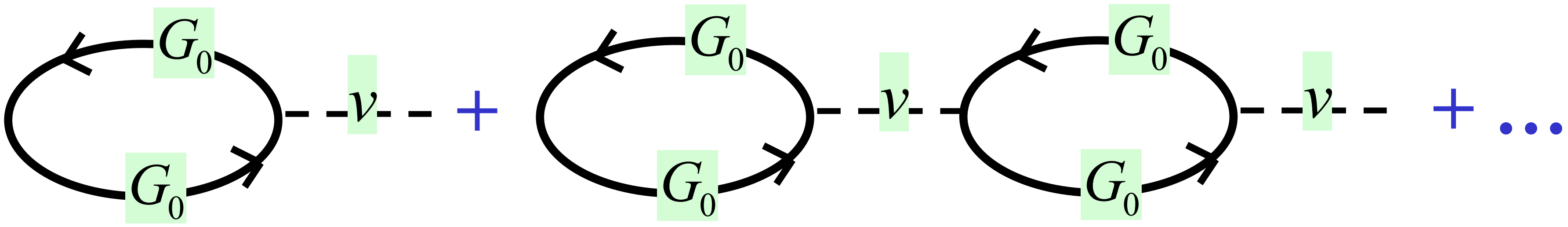
$|\mathbf{r}_j - \mathbf{r}_k|^{-1}$

$\delta V^1 =$



$\delta\phi_i = \delta V_i^0$ induces δV_i^1. δV_i^1 induces δq_j^1 which induces δV_i^2 and so on

Sum $\delta V_i^1 + \delta V_i^1 + \delta V_i^2 + \delta V_i^3 + \ldots$



The total screening charge can be summed as a geometric series

$$\delta q = \sum_n \delta q^n = \left(1 + vP^0 + vP^0 vP^0 + \ldots\right) P^0\, \delta V^0 = \left(1 - vP^0\right)^{-1} P^0\, \delta V^0$$

$\delta V_i^0 = \delta\phi$

The Screened Coulomb interaction

The total potential is

$$\delta V^{\mathrm{tot}} \equiv \delta\phi + \delta V^{scr} = \sum_n \delta V^n = \left(1 - vP^0\right)^{-1} \delta\phi$$

The dielectric function is defined as the ratio

$$\varepsilon_{ij}^{-1} = \frac{\delta V_i^{\mathrm{tot}}}{\delta\phi}$$

← **Total potential**

← **External potential**

and therefore*

$$\varepsilon^{-1} = (1 - vP^0)^{-1}$$

$$\varepsilon = 1 - vP^0$$

with $P^0 = G^0 G^0$

*This expression continues to hold in the exact description of linear response, but the irreducible polarizability P is no longer the independent particle $P^0 = G^0 G^0$.

The screened Coulomb interaction W is the potential resulting from a test charge embedded in a medium, i.e. $\delta\phi_i = v = 1/r$.

Thus

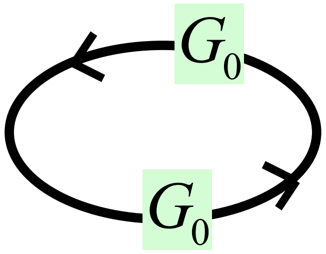
$$W = (1 - vP^0)^{-1} v = \varepsilon^{-1} v$$

GW: A Perturbation theory

Start from some non-interacting hamiltonian H_0.

1. $H_0 = -\frac{\nabla^2}{2} + V_{eff}(\mathbf{r},\mathbf{r}') \Rightarrow G_0 = \frac{1}{\omega - H_0}$ Usual: $H_0 = H^{\mathrm{LDA}}$

2. $\Pi = -i\,G_0 \times G_0$ RPA Polarization function

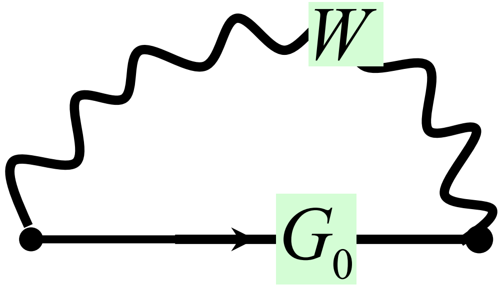


3. $W = \varepsilon^{-1} v = \left(1 - \Pi v\right)^{-1} v$

   $v(\mathbf{r},\mathbf{r}') = \left|\mathbf{r} - \mathbf{r}'\right|^{-1}$

   Dynamically screened exchange

4. $\Sigma = i\,G_0 W$ Self-energy $\Sigma =$



$$H(\mathbf{r},\mathbf{r}',\omega) = -\frac{\nabla^2}{2} + V^H(\mathbf{r}) + V^{ext}(\mathbf{r}) + \Sigma(\mathbf{r},\mathbf{r}',\omega)$$

This is V_{xc}

GW as Screened Hartree Fock

Hartree Fock: e^- senses an attractive potential V_x owing to correlated motion originating from antisymmetry that keeps e^- apart. Note: “correlation” is *usually* used as a term of art that means correlated motion not captured by Hartree Fock!

Write Fock exchange V_x in terms of Green’s functions:

$$\Sigma_\mathrm{x} = V_\mathrm{x}(\mathbf{r}) = i\int G(\mathbf{r},\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}' = iGv$$

GW: bare coulomb $v \rightarrow$ dynamically screened W:

$$V_\mathrm{bare}(\mathbf{r},\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|} \rightarrow W(\mathbf{r},\mathbf{r}',\omega) = \varepsilon^{-1}v; \quad \Sigma = iGW$$

Dynamical screening is the essential difference between GW and Hartree Fock. It make both qualitative and quantitative changes to the electronic structure.

Advantages of the GW Approximation

- The GW approximation can potentially redress the worst failings inherent in both Hartree-Fock and LDA:
- HF : nonlocality is present, but not screened (disaster)
- LDA: V is local (same for all e^-) ⇒ exact V has pathologies and effective one-particle ε_i, $\psi_i(\mathbf{r})$ are fictitious. Leads to many problems, e.g. cannot break time reversal symmetry.

- But … GW is a perturbation theory: first term in an expansion in W. Perturbation theory must be carried out around some starting point H_0. How choose H_0?

- Major development (Hybertsen and Louie, 1987): use LDA as starting point

$$H_0 = H^{\mathrm{LDA}} \Rightarrow G = G^{\mathrm{LDA}}, W = W^{\mathrm{LDA}} ; \Sigma = iG^{\mathrm{LDA}} W^{\mathrm{LDA}}$$

- Hugely successful in semiconductors

GW Approximation and Starting Point

G and Σ are usually generated from some effective noninteracting H_0. Usually $H_0 = H_{\mathrm{LDA}}$

But this is often problematic … particularly when magnetism is present

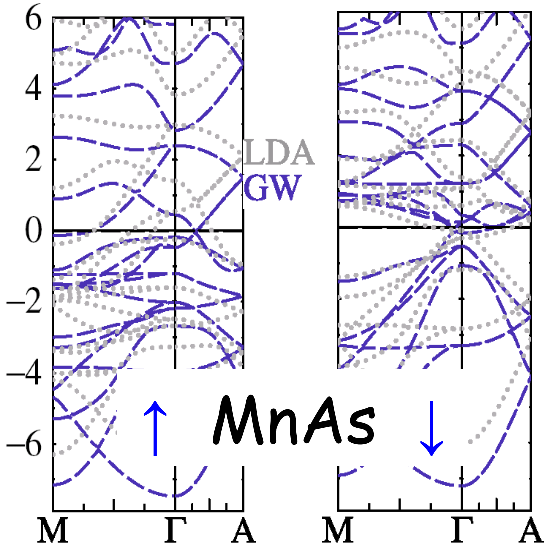
$$P(1,2) = -iGG, \quad \Sigma = iGW$$

GW neglects vertex

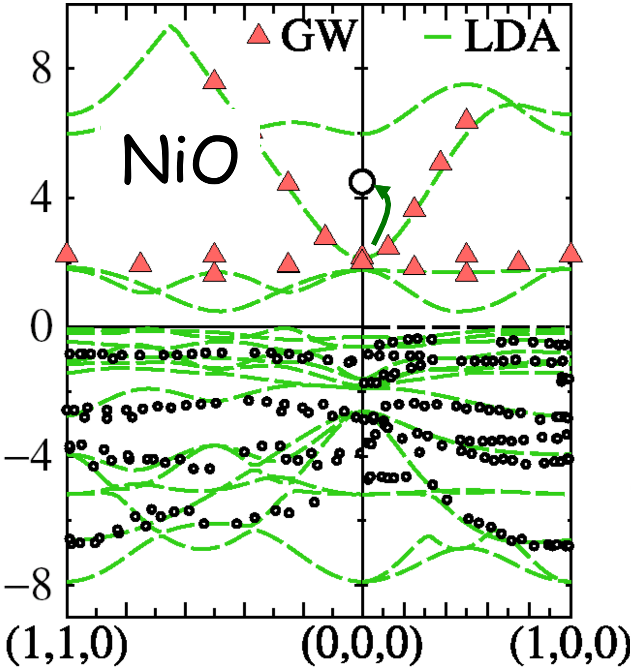
$$(h + V_H + V_{\mathrm{x}})\psi_s = \varepsilon_s \psi_s$$

$$G = \sum_s \frac{\psi_s \psi_s^*}{\omega - \varepsilon_s \pm i\delta}$$

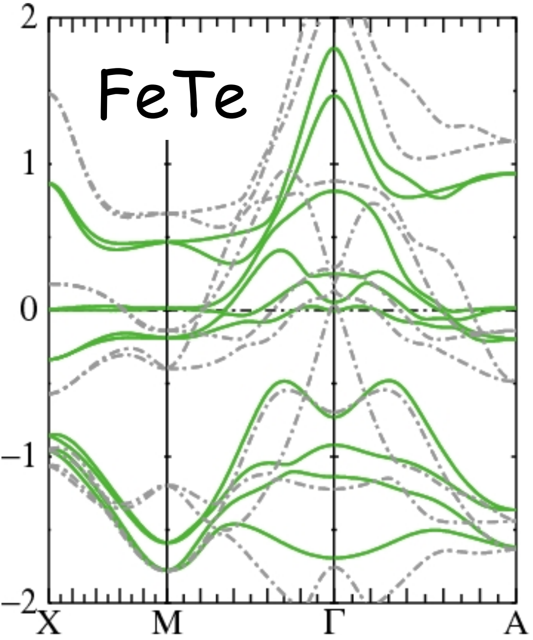
Nonsensical M, E_{x}



Severe gap errors



Nonsensical FS



Quasiparticle self-consistency

Idea: perform *GW* around some optimally chosen G_0.

Start with some trial V^{xc} (e.g. from LDA, or …). Defines G_0 :

$$H_0 = \frac{-1}{2m}\nabla^2 + V^{\mathrm{ext}}(\mathbf{r}) + V^{\mathrm{H}}(\mathbf{r}) + V^{\mathrm{xc}}(\mathbf{r},\mathbf{r}')$$

$$H_0\psi_i = E_i\psi_i \longrightarrow G_0(\mathbf{r},\mathbf{r}',\omega) = \sum_i \frac{\psi_i(\mathbf{r})\psi_i^*(\mathbf{r}')}{\omega - E_i}$$

GWA determines ΔV and thus H :

$$G_0 \xrightarrow{RPA} \varepsilon(iG_0G_0) \xrightarrow{GWA} \Sigma(\mathbf{r},\mathbf{r}',\omega) = iG_0W; \qquad \Delta V = \Sigma - V^{\mathrm{xc}}$$

Find a new V^{xc} that minimizes norm N, a measure of $\Delta V\, G_0$.

$$V^{\mathrm{xc}} = \frac{1}{2}\sum_{ij} \langle\psi_i|\mathrm{Re}\big(\Sigma(E_i)+\Sigma(E_j)\big)|\psi_j\rangle \qquad \text{result of min } N$$

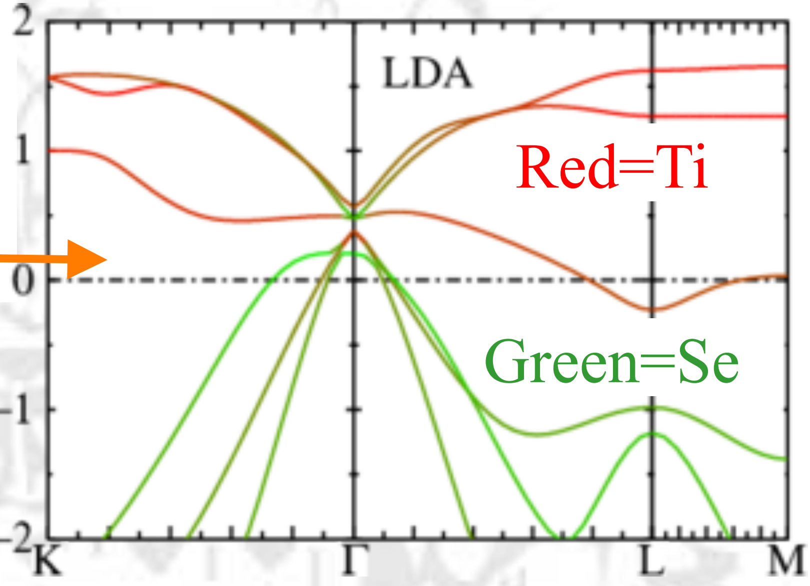
Iterate to self-consistency.

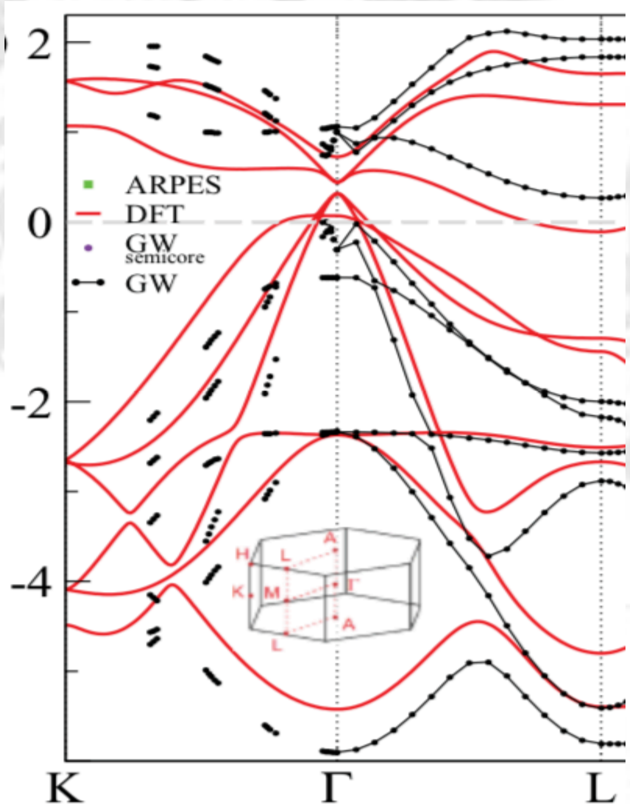
At self-consistency, E_i of G matches E_i of G_0 (real part).

Why Self-Consistency is necessary: $TiSe_2$

At RT, $TiSe_2$ has a simple unit cell. The gap is not reliably known, but it is thought to be < 0.05 eV.

LDA predicts inverted gap





Cazzaniga et al PRB 85 '12 added GW corrections to LDA ($G^{LDA}W^{LDA}$). Found an insulator with a gap ~0.5 eV … suggests usual problem with LDA

Renormalization by density

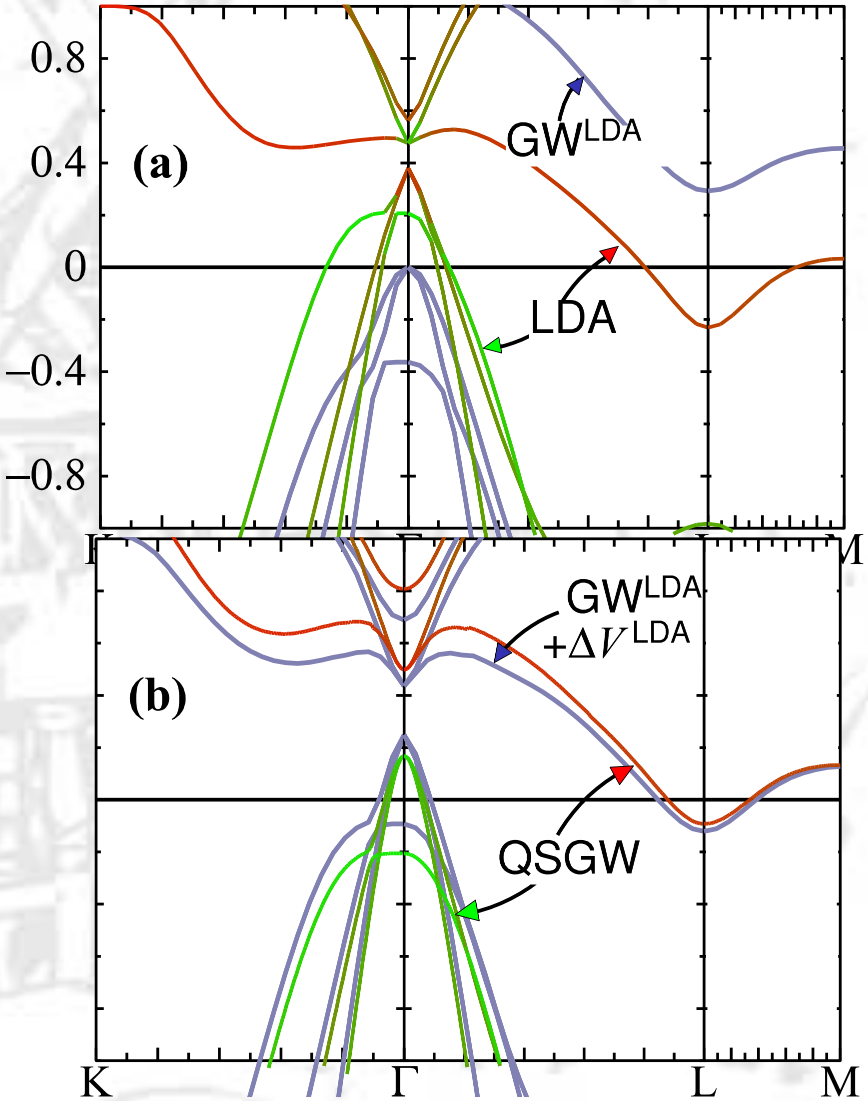
But the positive gap is an artifact of $G^{LDA}W^{LDA}$!

LDA and GW eigenfunctions should be different (missing in 1st order pert theory)

Off-diagonal self-energy $\Sigma^{nn'}$ modifies density $n(\mathbf{r})$ and thus V. Simple ansatz: assume LDA adequately yields $\delta V/\delta n$. The potential becomes

$$\Sigma - V_{xc}^{LDA}[n^{LDA}] + V_{xc}^{LDA}[n^{GW}]$$

Redo self-consistency.
Gap becomes negative again!

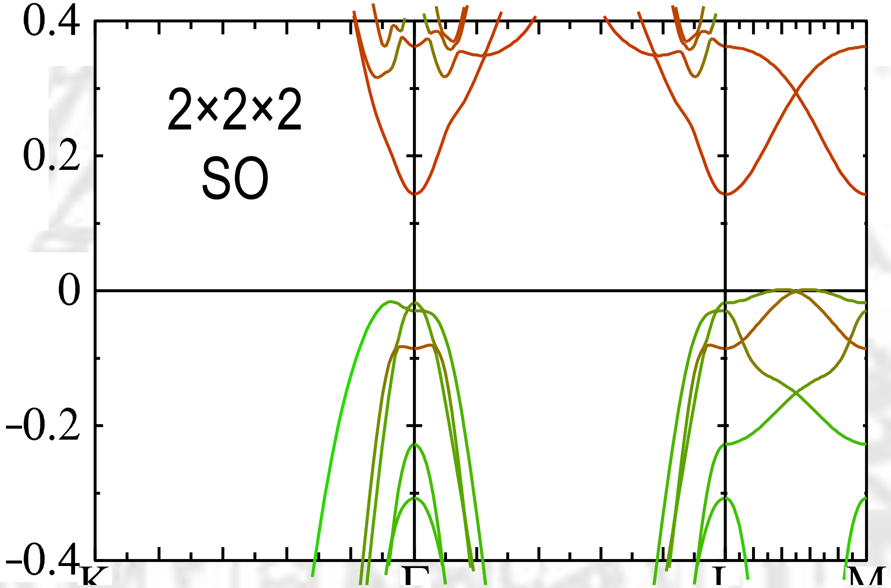


Result similar to QSGW

CDW-induced metal-insulator transition

At low T° $TiSe_2$ reconstructs into a 2 × 2 × 2 superstructure, a superposition of three L point phonon modes, forming a "3Q" charge density wave.

3Q is thought to have a gap Between 0.05 and 0.15 eV.



What does QSGW predict for CDW? Take displacement amplitudes from from GGA (Bianco et al PRB 92 '15).

Trace a path from ideal to 3Q geometry.
Bands evolve in a tortuous manner … but at CDW geometry, QSGW predicts an insulator, $E_G = 0.17$ eV (including spin-orbit)

What we learn: $\delta V/\delta n$ is important, not captured by $G^{LDA}W^{LDA}$

Important Source of Strong Correlations: Spin

LDA description of Ni, Fermi liquid regime

Classic ARPES study: Himpsel, Knapp, Eastman PRB 19, 2919

Exchange splitting:

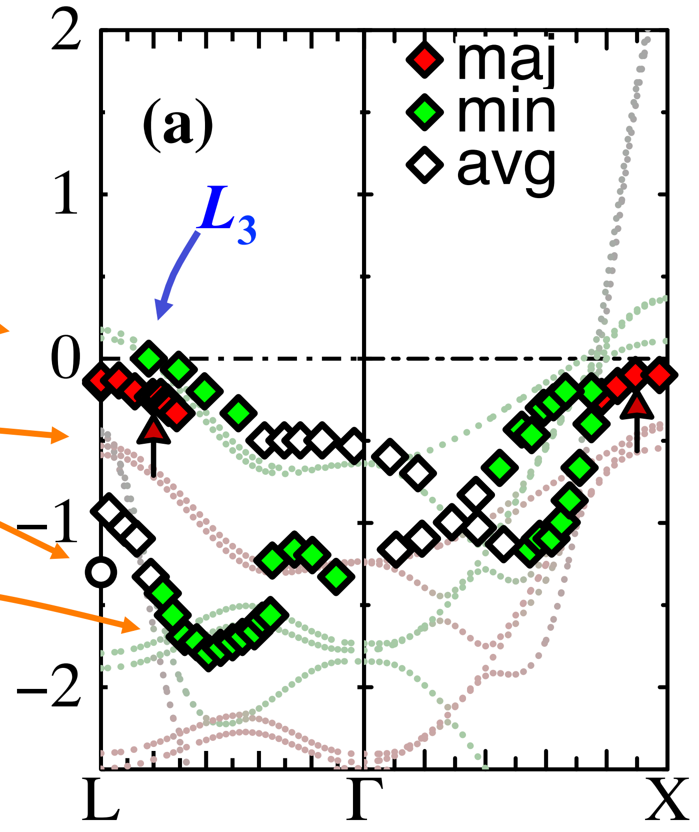
$\Delta E_x = L_{3\downarrow} - L_{3\uparrow} \approx 0.3\ \mathrm{eV}$

0.6 eV in LDA

s band wrongly placed

Poor dispersion in Λ_1 band

LDA predicts M=0.6 μ_B, close to expt. But … we shall see good agreement is fortuitous



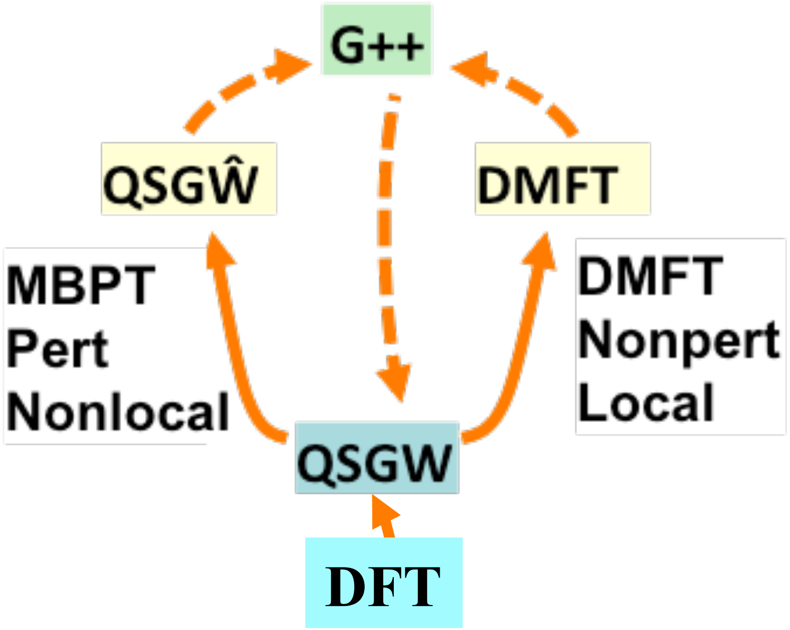
No satellite at -5 eV

QSGW also not sufficient ⋯ discuss more tomorrow

Questaal's Hierarchy

Basic code (lmf) : all electron implementation of DFT

GW code (lmgw, lmgwsc) : Uses lmf basis set to implement GW and QSGW



G++

QSGŴ

DMFT

MBPT
Pert
Nonlocal

DMFT
Nonpert
Local

QSGW

DFT

Beyond GW: two routes:

(1) Many-body pert theory. Add ladders to W (Myrta and Brian)
Works very well when spin fluctuations are not large

(2) QSGW+Dynamical Mean Field theory (Swagata and Francois)
Needed when spin fluctuations are strong

G++ : properties from two-particle G + BSE : spin and charge susceptibilities (Brian, Swagata), electron-phonon interaction (Savio)

Questaal's Implentation of DFT

- ✔ Different implementations of DFT, Survey
- ✔ All-electron methods; how augmentation works
- ✔ Linearization ⇒ energy-independent basis
- ✔ lmf : All-electron Full Potential method
- ✔ Jigsaw Puzzle Orbitals
- ✔ Two particle basis sets for many-body theory

Practical Implementations of the LDA

Single-particle orbitals ψ_i are expanded in some basis set. Many ways to do this.

Classification #1: ψ_i are expanded in plane waves (most common), or in short-range, atom-centered orbitals.

Questaal uses the latter.

Classification #2: orthogonalization to the core. *Either*:

Replace the core by an effective (pseudo)potential, *or*

Keep all electrons: Augment the wave functions in spheres around each nucleus with numerical solutions of the radial Schrodinger equation. Originally formulated by Slater

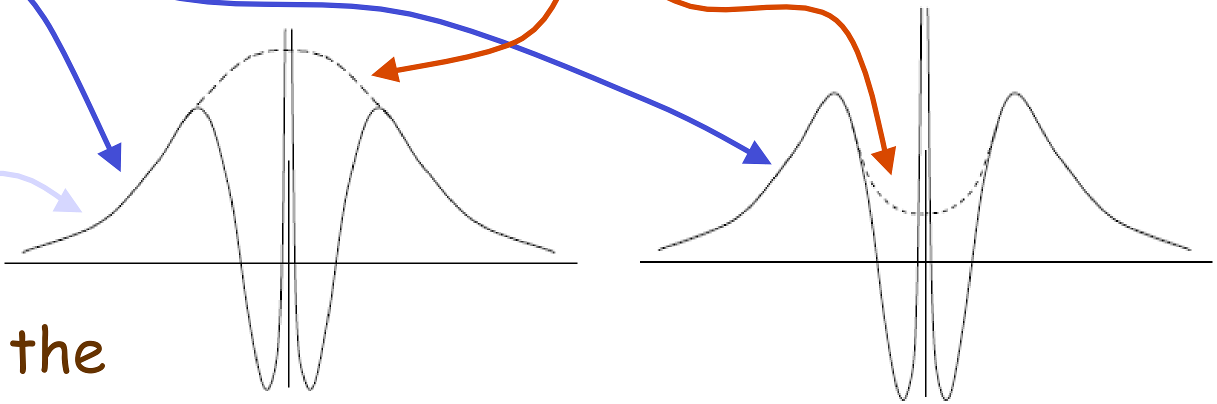
Questaal is an all-electron method

Pseudopotentials (most common)

Add some artificial, or pseudo-potential V^{PS} to V^{LDA} ⇒ replace true wave function ψ with smooth analog of ψ^{PS}, with the same eigenvalues.

No core!

V^{PS} is not unique!

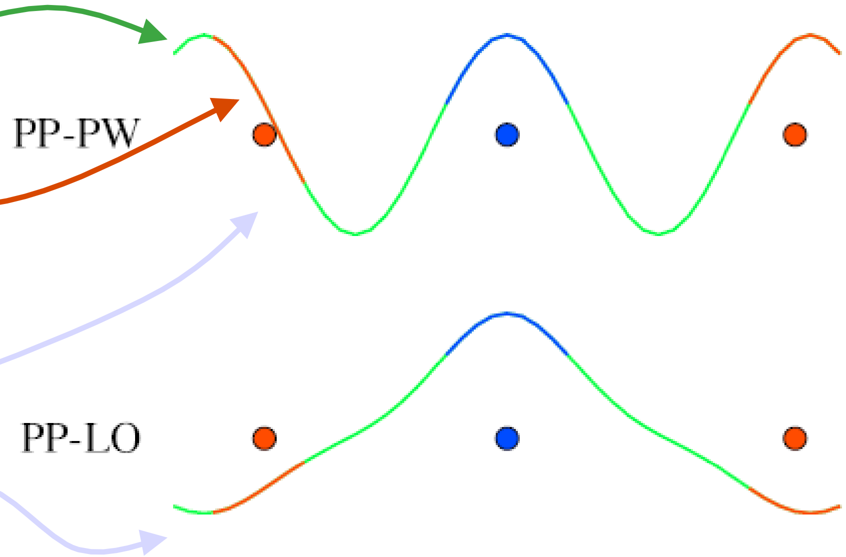


The envelope defines the basis.

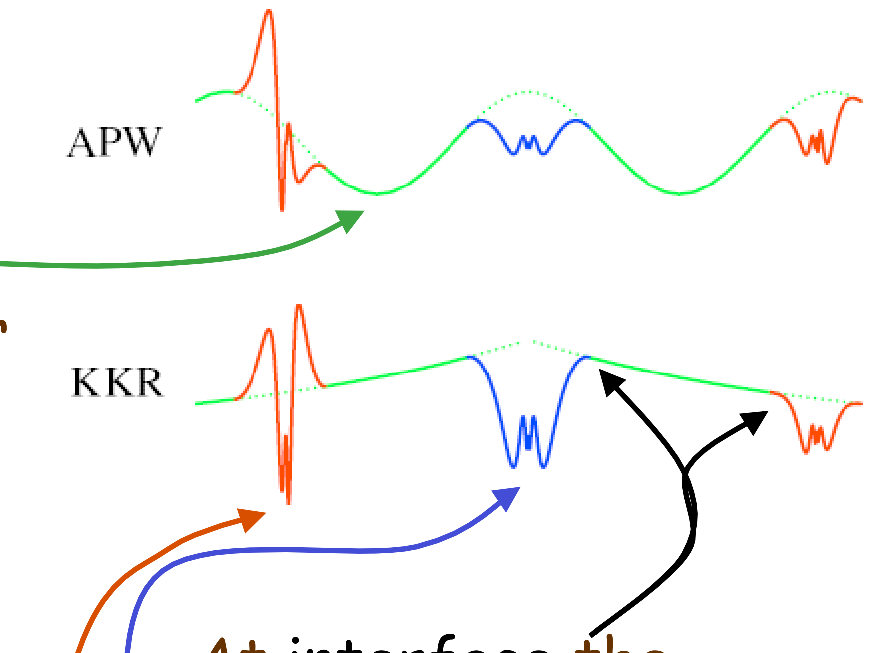
Shown here as green.

Blue, red show augmentation region : region where $V^{\mathrm{PS}} \neq 0$.

Can be Plane Waves, or Atom-centered functions



Augmentation



All-electron basis sets begin with envelope functions :

Far from nuclei ψ is smooth and described by smooth envelopes. They can be either plane waves or local functions.

Valence ψ must be orthogonal to core states ⇒ many wiggles that envelope functions cannot well represent.

Solution: augment spheres around nucleus with numerical solutions of the Schrodinger equation (red, blue). Called partial waves.

At interface the augmented functions must match continuously and differentiably onto the envelopes.

Both value and slope must match ⇒ quantization condition (see later).

Four basic variants

4 types depicted in figure.

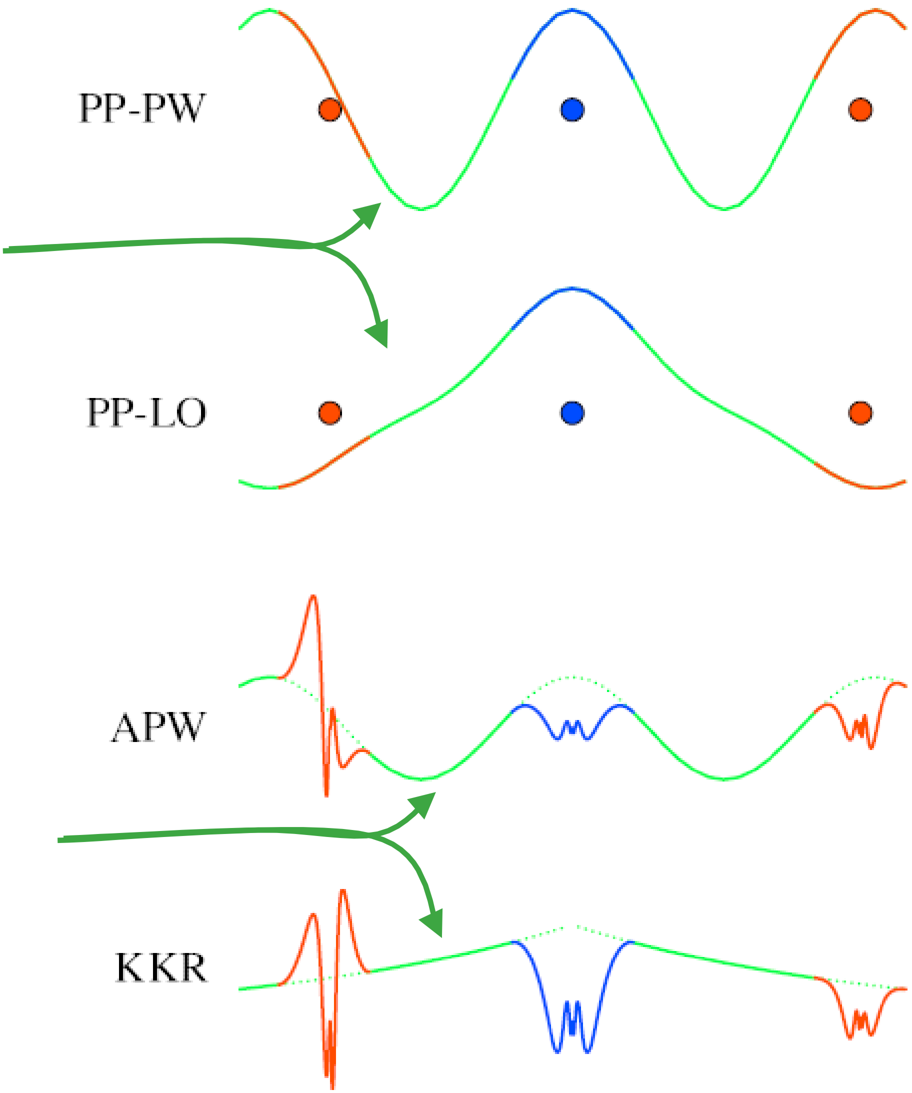
Envelope functions are green.
Blue, red show augmentation region

Pseudo functions:
- ☑ Very efficient
- ☒ Approximation can be an issue

All-electron :
- ☑ Most rigorous (e.g. semicores)
- ☒ More cumbersome

Plane waves:
- ☑ Readily made complete
- ☒ Not localized

Atom centered functions:
- ☑ Efficient, physical intuition
- ☒ Completeness can be an issue



Energy dependence

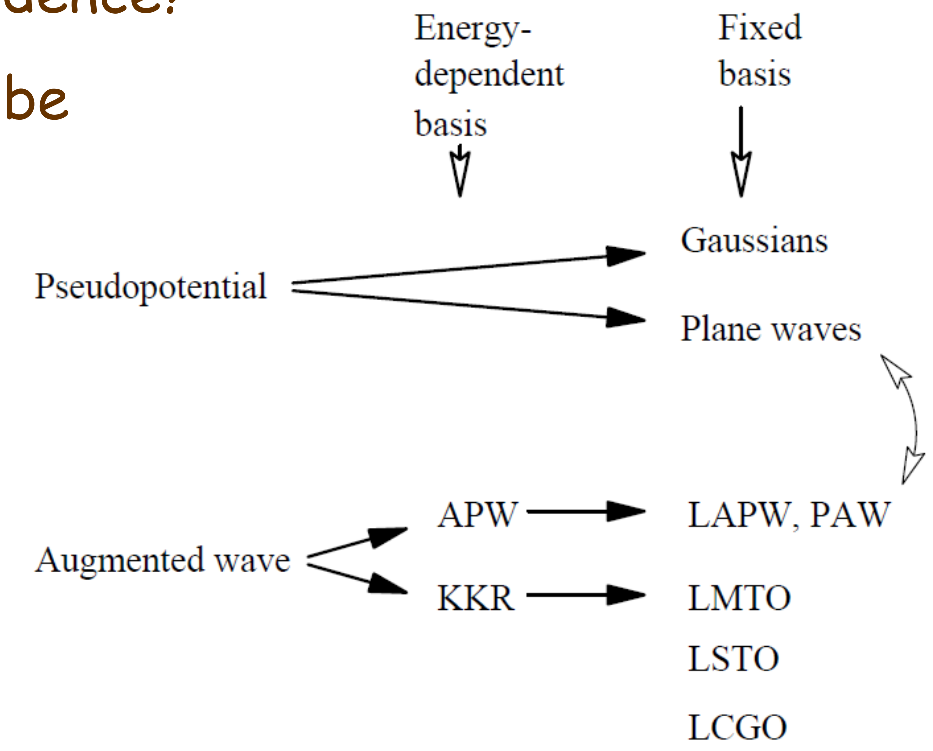
$\psi = \psi(E,\mathbf{r})$. What about E dependence?

Classification #3: the basis can be

(1) Fixed (PP methods) -- simplest

(2) potential-and-energy dependent (KKR,APW). Accurate but expensive. (Nonlinear eigenvalue problem; see later)

(3) potential dependent.
LAPW = linearized APW
LMTO = linearized KKR



Linearization turns nonlinear secular matrix into linear algebraic eigenvalue problem, like fixed-basis case (later).

Modest loss of accuracy with large efficiency gains.

Augmentation: Muffin-tin potential and partial waves

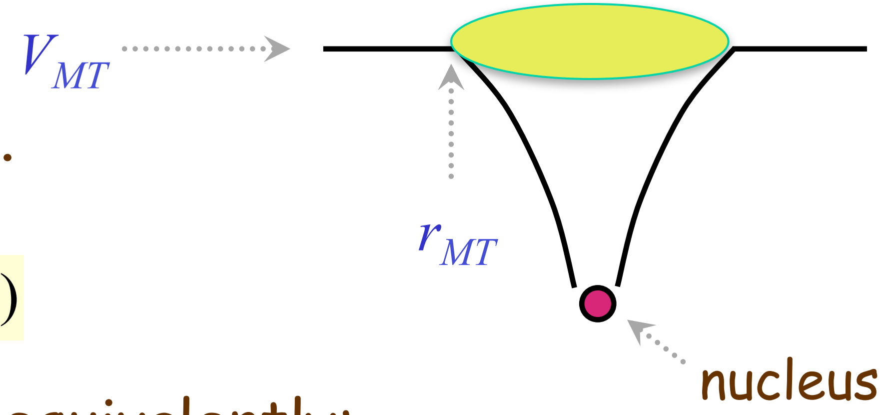
Cut and paste approach to Schrödinger equation

MT potential: spherically symmetric inside sphere (called "augmentation" sphere)
Constant in between

Construct basis function χ_j piecewise:

Consider the MT part. l and m are good quantum numbers; use L as a shorthand for compound (l,m) indices. The SE separates and:

$$\Phi_L(\varepsilon,\mathbf{r}) = Y_L(\hat{\mathbf{r}})\phi_l(\varepsilon,r)$$

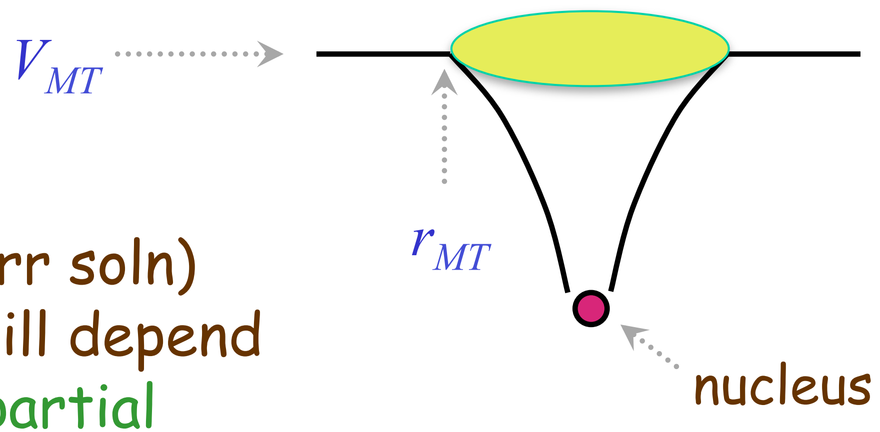


ϕ_l satisfies $(-\nabla^2 + V(r))\phi_l = \varepsilon\phi_l$ or equivalently:

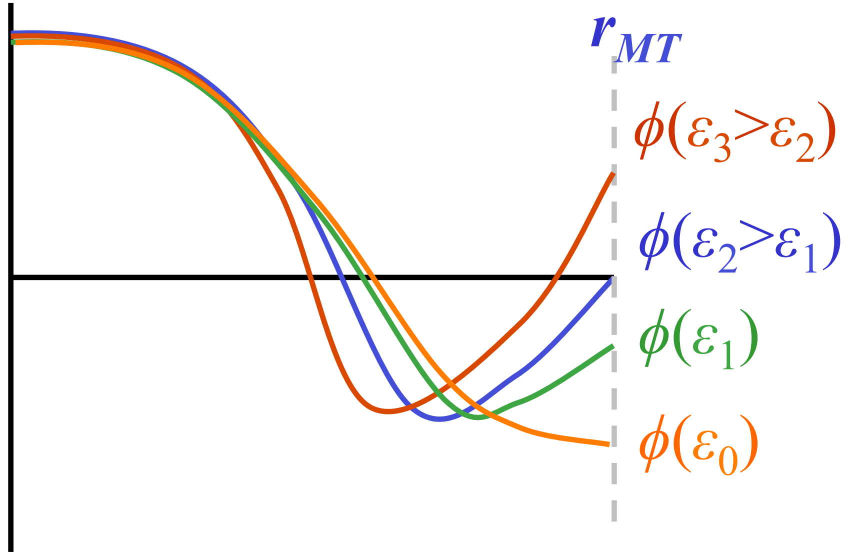
$$\left(-\frac{d^2}{dr^2} + V(r) + \frac{l(l+1)}{r^2} - \varepsilon\right) r\phi_l(\epsilon,r) = 0$$

The $\phi_l(\varepsilon,r)$ are called partial waves

Partial Waves and Boundary conditions

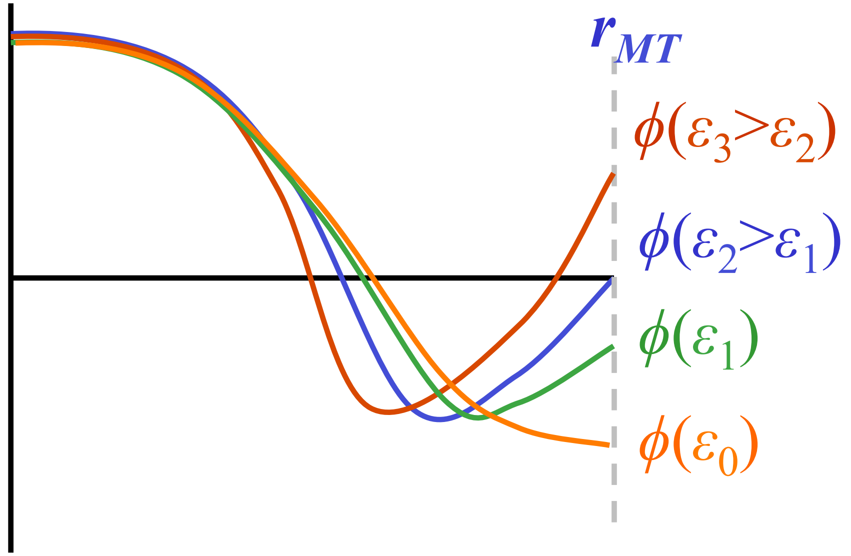


2nd order differential equation ⇒ two solutions.
Also two boundary conditions:
1. $\phi_l(r)$ regular as $r \to 0$ (eliminate irr soln)
2. The boundary condition at r_{MT} will depend on the whole crystal. Φ_l is called a partial wave because we have yet to specify the boundary condition at $r = r_{MT}$.



As ε increases, $\phi_l(\varepsilon, r)$ acquires more curvature ⇒ BC changes. Thus specifying ε completely fixes the remaining degree of freedom of the partial wave.

Logarithmic Derivative



At $\varepsilon = \varepsilon_0$, slope < 0

As ε increases, $(-\nabla^2)$ increases.

$\varepsilon_0 < \varepsilon < \varepsilon_1$: slope $\phi_l'(r) \to 0$

At $\varepsilon = \varepsilon_1$, $\phi_l(r) \to 0$

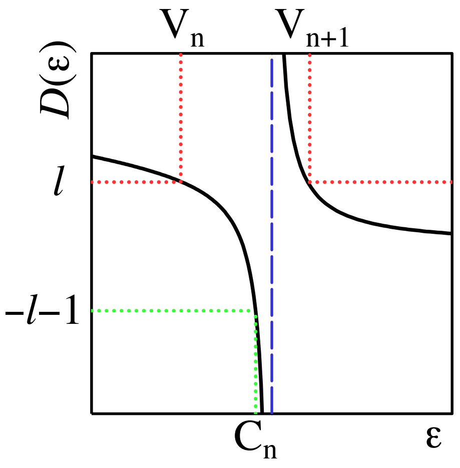
At $\varepsilon = \varepsilon_2$ $\phi_l(r)$ gets extra node

Information neatly encapsulated in the logarithmic derivative D at r_{MT}

$$D\{\phi_l(\varepsilon)\} = \left.\frac{r \cdot d\phi_l(\varepsilon)}{\phi \cdot dr}\right|_{r_{MT}} = \left.\frac{d \ln \phi_l(\varepsilon)}{d \ln r}\right|_{r_{MT}}$$

$D\{\phi_l\}$ is an ever-decreasing function of ε. A pole appears whenever principal quantum number changes.

Value $\varepsilon = V_l$ at $D = l \sim \Rightarrow$ band bottom
Value $\varepsilon = C_l$ at $D = -l-1 \Rightarrow$ band centre

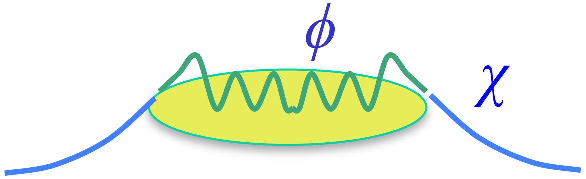


APW and KKR Methods

The $\phi_l(\varepsilon,r)$ join smoothly onto envelope functions in the interstitial.

Envelope function χ_j is “augmented” by $\phi_l(\varepsilon,r)$ in each augmentation sphere.

χ_j can be any functions that are reasonably complete in the interstitial.



APW: Envelopes ⇒ plane waves $\chi_{\mathbf{G}} = e^{i(\mathbf{k}+\mathbf{G}).\mathbf{r}}$ as in the PW-PP method except $\chi_{\mathbf{G}}$ is augmented inside each MT sphere with partial waves.

KKR: Suppose the potential really is a MT. Then it is solved exactly:

$$(\nabla^2 + \varepsilon - V_{MT})\,\chi(\varepsilon,\mathbf{r}) = 0, \quad r > r_{MT}$$

Helmholz equation: solns Hankels H and Bessels J

Family of Hankel functions $H_{\mathbf{R}L}(\mathbf{r})=H_L(\mathbf{r}-\mathbf{R})$ at each site $\mathbf{R}$: makes a nearly exact, minimal basis for the muffin-tin potential.

This is the KKR Method.

Spherical Hankel and Bessel Functions

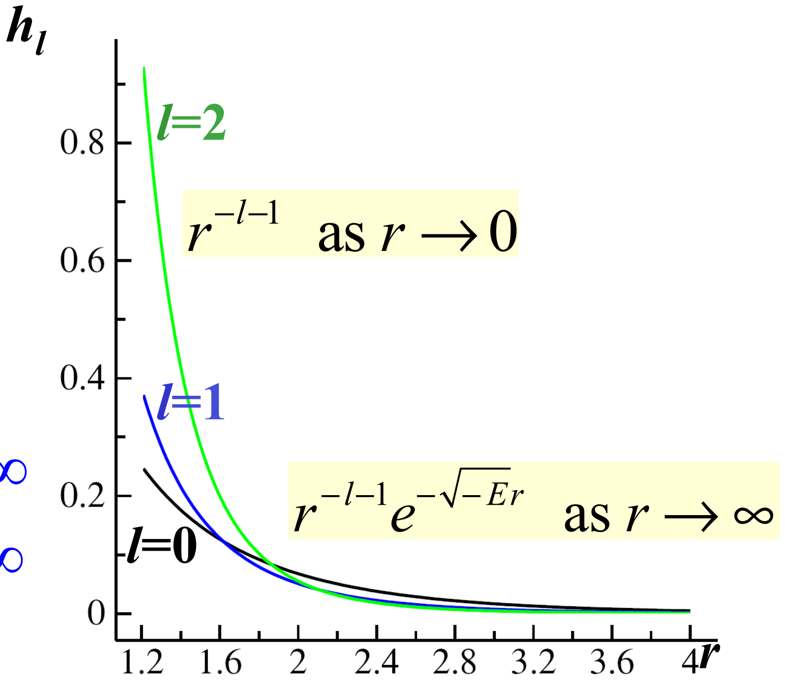
Spherical Hankel and Bessel functions satisfy this equation:

$$(\nabla^2 + E)\,\{H_L, J_L\}(E,\mathbf{r}) = 0, \qquad r \neq 0$$

$$\{H_L, J_L\}(E,\mathbf{r}) = \{h_l, j_l\}(E,r)\,Y_L(\hat{\mathbf{r}})$$

Radial part

Factor out angular dependence



r^{-l-1} as $r \to 0$

$r^{-l-1} e^{-\sqrt{-E}r}$ as $r \to \infty$

Hankels: singular as $r \to 0$, regular as $r \to \infty$

Bessels: regular as $r \to 0$, singular as $r \to \infty$

$$h_l(E,r) \to r^{-l-1} e^{-\sqrt{-E}r} \quad \text{as } r \to \infty$$

$$j_l(E,r) \to r^{l} e^{+\sqrt{-E}r} \quad \text{as } r \to \infty$$

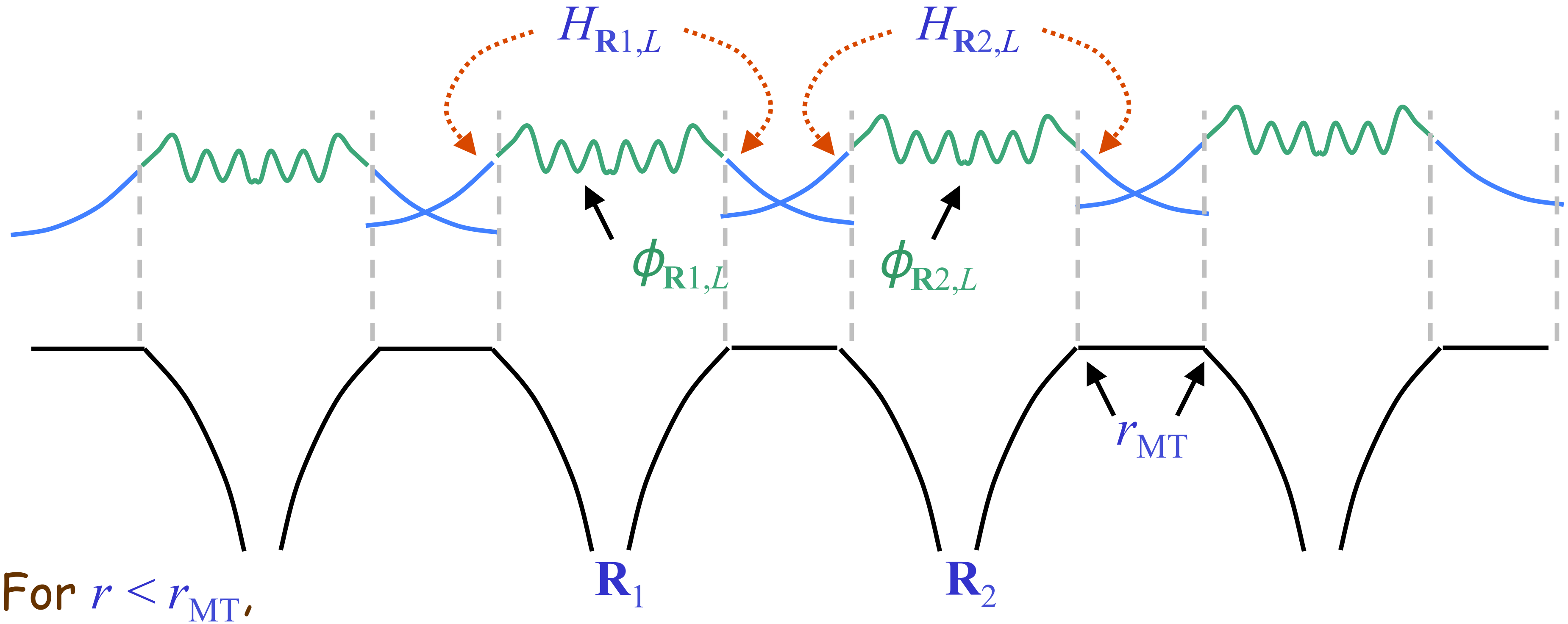
Hankels can be expanded as a linear combination of Bessels around a remote site. Called a one-center expansion:

$$H_L(E,\mathbf{r}-\mathbf{R}) = \sum_{L'} S(\mathbf{R}-\mathbf{R}', E)\, J_{L'}(E,\mathbf{r})$$

Structure constants

KKR method in a nutshell

In the interstitial, solutions are linear combinations of atom-centered Hankel functions $H_{\mathbf{R}L}$ centered at each nucleus $\mathbf{R}$.



For $r < r_{\mathrm{MT}}$,

$$\Phi_{\mathbf{R}L}(\mathbf{r}) = \sum\nolimits_{\mathbf{R}L} C_{\mathbf{R}L}\phi_{\mathbf{R}l}(\varepsilon,r)Y_L(\widehat{\mathbf{r}-\mathbf{R}}),$$

We have piecewise solutions of the SE, with kinks matching $H_{\mathbf{R}L}$ at r_{MT}.

To satisfy boundary conditions, kinks must disappear

Linear Methods in Band Theory

Problem …

APW & KKR ⇒
energy dependent
hamiltonians.

Resolved by
linearization

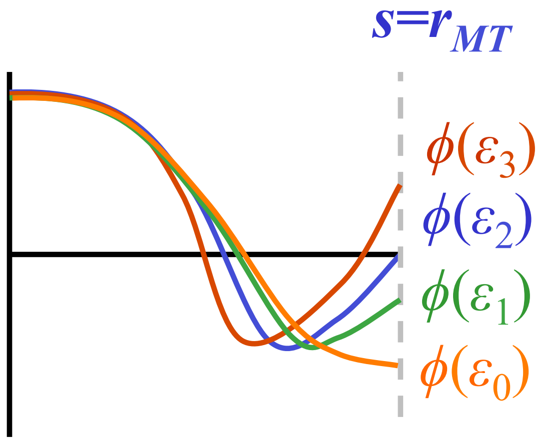
Ole Krogh Andersen

KKR excepted, nearly all
modern electronic
structure methods use
linearization in some way

6,500 citations

- Linear methods in band theory O. K. Andersen Phys. Rev. B 12, 3060 (1975)
- Explicit, First-Principles Tight-Binding Theory, O. K. Andersen and O. Jepsen Phys. Rev. Lett. 53, 2571 (1984). See also Phys. Rev. B 34, 5253 (1986)
- Muffin-tin orbitals of arbitrary order, O. K. Andersen and T. Saha-Dasgupta Phys. Rev. B 62, R16219 (2000) and also chapter in Electronic Structure and Physical Properties of Solids. The Use of the LMTO Method. Easiest-to read but predecessor of NMTO: Tank & Arcangeli, Phys. Stat. Sol. (b) 217, 89

Linearization



Key observation: partial wave $\phi_l(\varepsilon,r)$ in sphere varies smoothly and slowly with energy

$$\phi_l(\varepsilon,r)=\phi_l(\varepsilon_\nu,r)+(\varepsilon-\varepsilon_\nu)\dot{\phi}_l(\varepsilon,r)+\ldots$$

Energy dependence parameterized by log derivative function

$$D\{\phi_l(\varepsilon)\}=d\ln\phi_l(\varepsilon)/d\ln r$$

Or by potential function (they are related)

$$P\{\phi_l(\varepsilon)\}=W\{\phi_l(\varepsilon),h_l\}/W\{\phi_l(\varepsilon),j_l\}$$

Linearize $\phi_l(\varepsilon)$ kink-cancellation ⇒ linear algebraic eigenvalue problem

APW → LAPW; KKR → LMTO

Gold standard **Efficient**

Present version of Full-Potential LDA code (lmf)

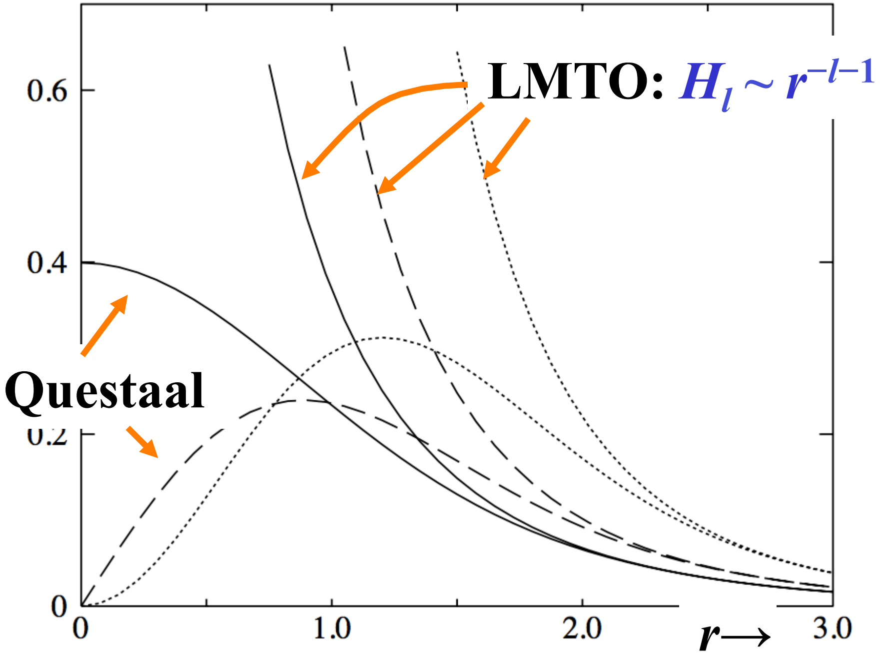
All-electron LDA code

1. Unique basis functions:
smooth Hankel functions
   Smooth & regular at origin
   Accurate, small basis

2. Novel Augmentation similar in philosophy to PAW but keeps rigor of LAPW

3. APW's may be included: fusion of MTO+APW.
PRB81, 125117 (2010)

4. Front end for GW, QSGW


LMTO: $H_l \sim r^{-l-1}$

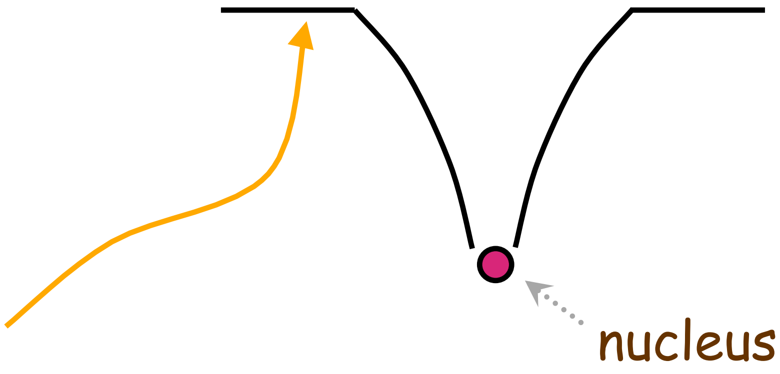
Questaal

Smooth Hankel Functions I

Regular Hankel functions :

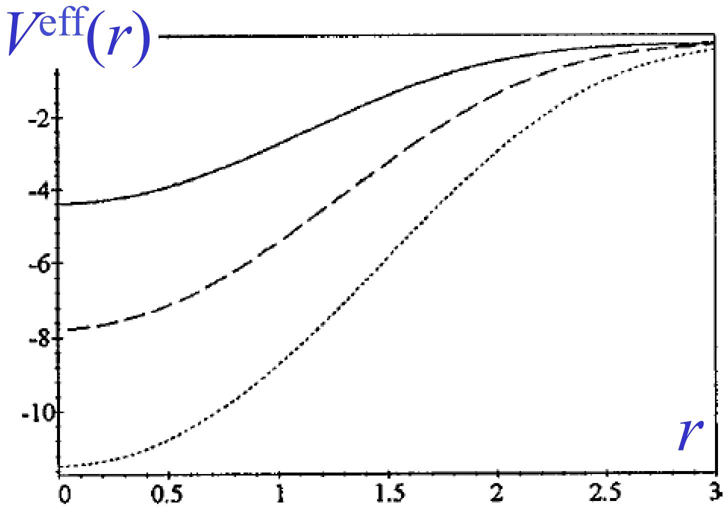
- $\propto 1/r^{l+1}$ for small r …
  singularity hard to manage
- are "too stiff" : real $V(r)$ is not flat in interstitial. It would be better if χ satisfied a SE

$$(-\nabla^2 + V^{\mathrm{eff}}(r) - E)\,\chi(E,\mathbf{r}) = 0$$



with $V^{\mathrm{eff}}(r)$ approaching a constant smoothly. Functions $\mathcal{H}_L$ are solutions to this equation

$$(-\nabla^2 - E)\,\mathcal{H}(E,r_s;\mathbf{r}) = 4\pi G_L(r_s;\mathbf{r})$$



solve a "Schrodinger equation" with

$$V^{\mathrm{eff}}(r) = -4\pi \frac{G_L(r_s;r)}{H_L(E,r_s;r)}$$

The smoother G is, the smoother V^{eff}.

Smooth Hankel Functions II

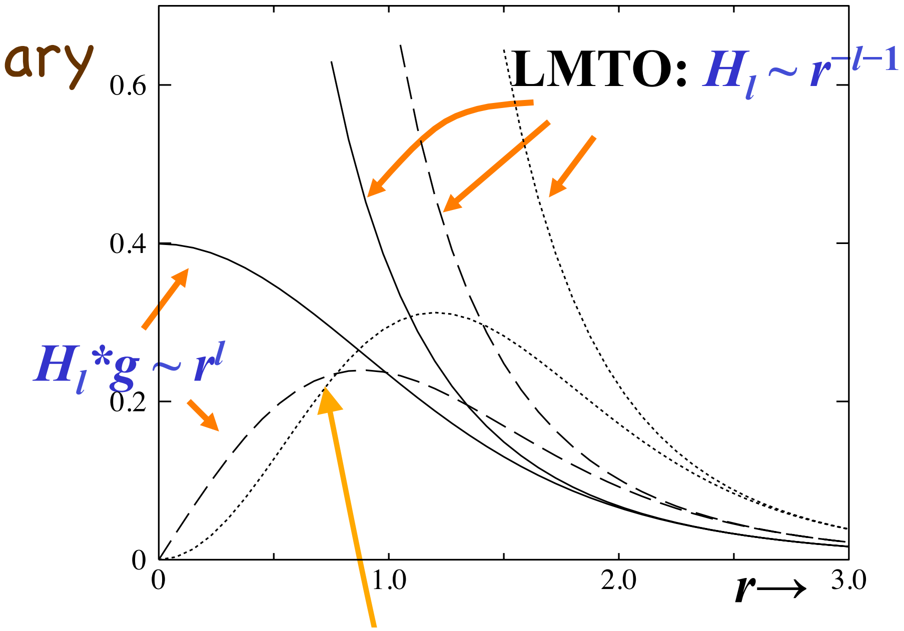
The $\mathcal{H}_L$ are smooth Hankel functions

The Fourier transform of an ordinary Hankel function is

$$\hat{H}_L(E;\mathbf{q}) = \frac{-4\pi(iq)^l Y_L(i\mathbf{q})}{E-q^2}$$

The FT of $\mathcal{H}_L$ is the product of H_L and a Gaussian g:

$$\hat{\mathcal{H}}_L(E,r_s;\mathbf{q}) = \frac{-4\pi(iq)^l Y_L(i\mathbf{q})e^{-4r_s^2q^2}}{E-q^2}$$



J. Math. Phys. 39, 3393

In $\mathbf{q}$ space, g has a width $1/(4r_s)$ $\quad \hat{g}(r_s;\mathbf{q}) = e^{-4r_s^2q^2}$

In $\mathbf{r}$ space, g has a width r_s $\quad g(r_s;r) = e^{-(r/r_s)^2}$

$\mathcal{H}_L(E,r_s;\mathbf{r})$ is a convolution of $H_L * g$ and is smooth everywhere

Augmentation

Standard LAPW and LMTO methods must augment (replace) the envelope function with radial solutions of the SE to very high l … something like $l=8$ to be accurate.

Curious … because pseudopotential l-cutoffs are ~2. Yet there is a connection between augmentation and pseudopotentials. Why?

lmf uses a unique form of augmentation.

The total density n is made of a superposition of 3 components:

1. Interstitial, or smooth density n_i . Not augmented!
   extends everywhere in space (analogous to PP or PAW method)
2. True density inside augmentation sphere $\mathbf{R}$, $n_{1\mathbf{R}L}$
3. 1-center (local) representation of the interstitial density, $n_{2\mathbf{R}L}$

$$n(\mathbf{r}) = n_i(\mathbf{r}) + \sum_{\mathbf{R}L}^{L_{\max}} \left\{ n_{1\mathbf{R}L}(\mathbf{r}) - n_{2\mathbf{R}L}(\mathbf{r}) \right\}$$

These approximately cancel
Inside augmentation spheres

Augmentation II

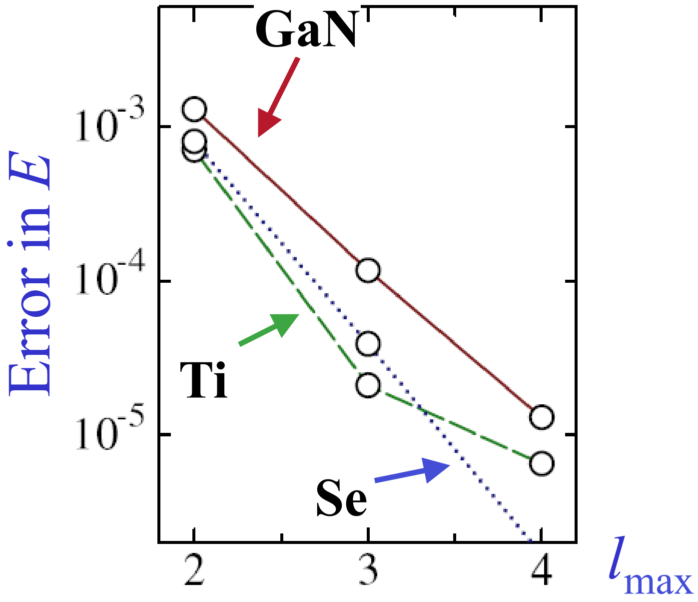
The potential has a similar "three-component" representation

$$V(\mathbf{r}) = V_i(\mathbf{r}) + \sum_{\mathbf{R}L}^{L_{\max}} \left(V_{1\mathbf{R}L}(\mathbf{r}) - V_{2\mathbf{R}L}(\mathbf{r}) \right)$$

Each potential is computed (almost) independently of the others:

V_i is calculated from n_i only
$V_{1\mathbf{R}}$ is calculated from $n_{1\mathbf{R}}$ only
$V_{2\mathbf{R}}$ is calculated from $n_{2\mathbf{R}}$ only

No cross terms!



Why is this better?

- ➢Cross terms are unwieldy
- ➢L convergence much faster than standard LAPW
- ➢Makes connection betw/ PP, PAW, and all-electron methods.

Local orbitals

Recall energy linearization common to (nearly) all methods

$$\Phi_{\mathbf{R}L}(\varepsilon,\mathbf{r})=\phi_{\mathbf{R}l}(\varepsilon,\mathbf{r})Y_{\mathbf{R}L}(\hat{\mathbf{r}})$$

$$\phi_{\mathbf{R}l}(\varepsilon,\mathbf{r})\approx\phi_{\mathbf{R}l}(\varepsilon_v,\mathbf{r})+(\varepsilon-\varepsilon_v)\dot{\phi}_{\mathbf{R}l}(\varepsilon_v,\mathbf{r})+\ldots$$

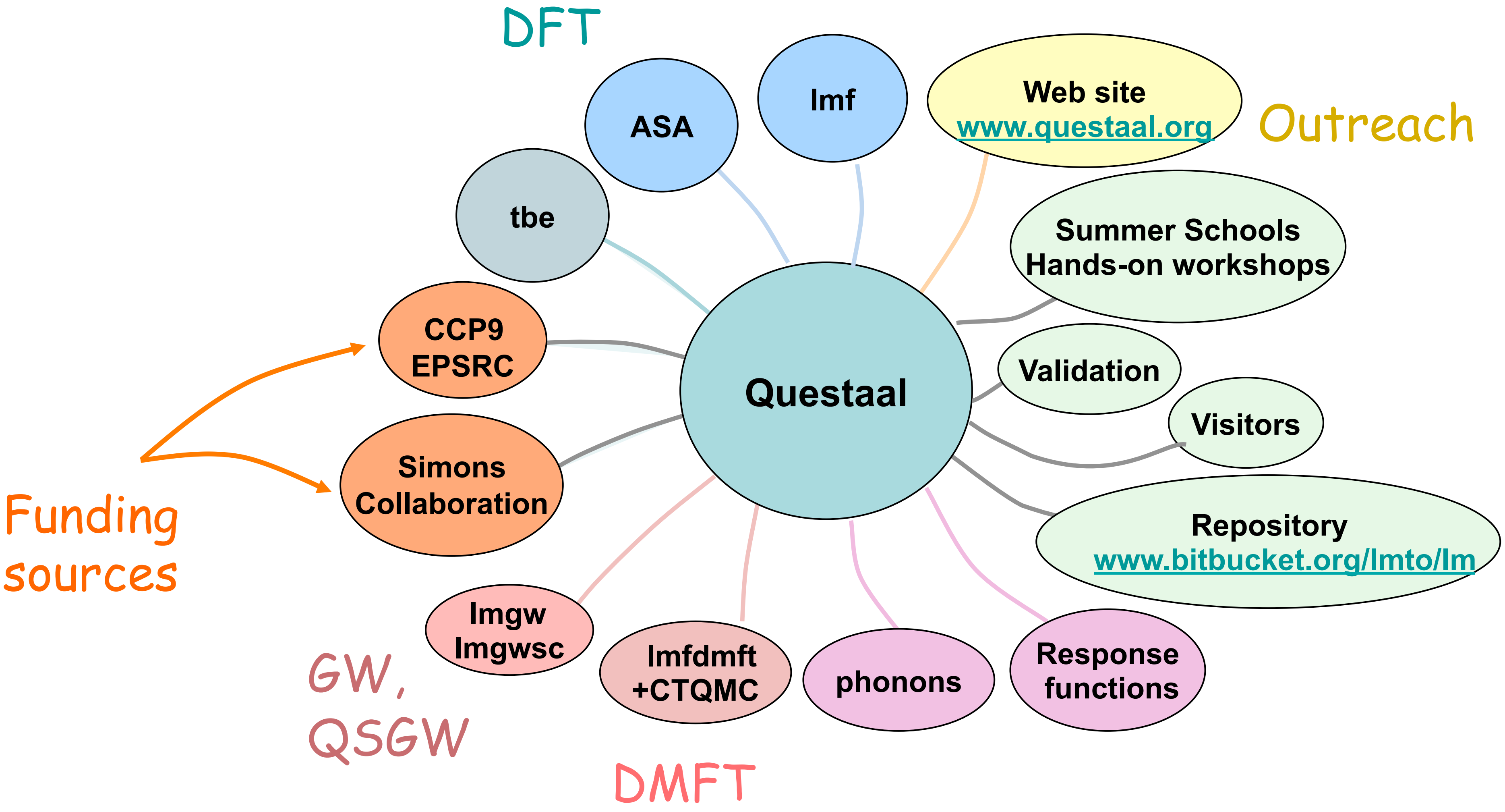
Standard: In the LMTO method (and LAPW) methods we add new augmentation orbitals $\phi_{\mathbf{R}L}=\phi_{\mathbf{R}L}(\varepsilon_v,r)$ and $\partial\phi_{\mathbf{R}L}/\partial\varepsilon$. Procedure:

1. Integrate $\phi_{\mathbf{R}L}(\varepsilon_z,r)$ at some ε_z
2. Subtract $a\times\phi_{\mathbf{R}L}+b\times\partial\phi_{\mathbf{R}L}/\partial\varepsilon$ from $\phi_{\mathbf{R}L}(\varepsilon_z,r)$ to make both value, slope vanish at r_{MT} . The resulting "local orbital" is completely confined to the augmentation sphere.
3. Add this orbital to the basis set. Extends range of energy window which solves SE, and the cost of a larger basis.

Important for high-accuracy calculations, esp GW

CCP9 Flagship: Questaal suite

Questaal is the previous CCP9 flagship (www.questaal.org)
It is an integrated electronic structure package that combines:



Descendant of the Stuttgart LMTO method

Problem …

APW & KKR ⇒ energy dependent hamiltonians.

Resolved by linearization

Ole Krogh Andersen

Andersen formulated the LMTO and LAPW methods.
O. K. Andersen Phys. Rev. B 12, 3060 (1975).
Pseudopotentials are also based on an (approximate) linearization!

Original LMTO-ASA was developed for the Stuttgart group.

Package formed the backbone of many developments :

- LDA+U (Aninismov)
- Exact exchange (Kotani)
- All-electron GW (Aryasetiawan)
- Electron-phonon interactions, superconductivity (Lichtenstein)

Full-potential version developed by Methfessel and MvS.
Full-Potential GW, QSGW developed by Kotani, Faleev, MvS.

Functionality

DFT

- Efficient basis set (Pashov)
- Magnetic linear response, CPA

GW

- Add diagrams (Gruening, Cunningham)
- Improve efficiency (Pashov, Lueders)
- Schemes to improve accuracy

Phonons

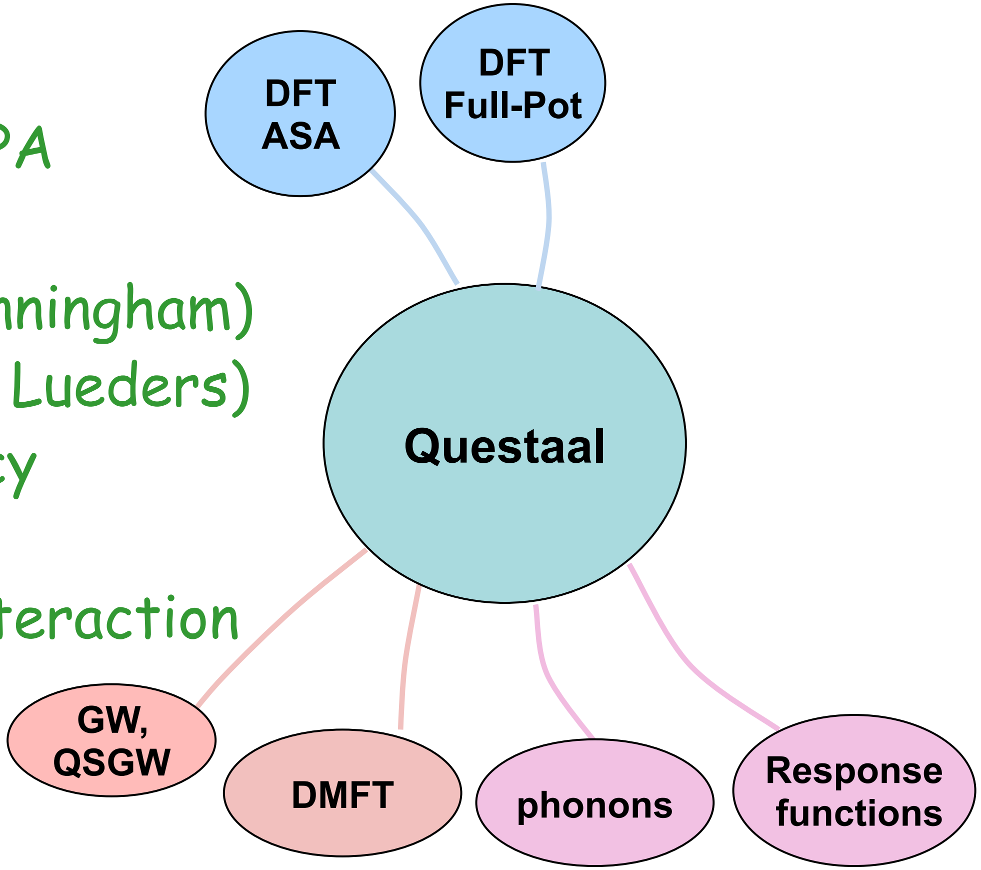
- Phonons, electron-phonon interaction in GW (Bononi, Laricchia)

QSGW+DMFT

- Acharya and Jamet

Response functions (BSE)

- Optical response, some magnetic susceptibility in MBPT
- Magnetic and spin susceptibility in DMFT

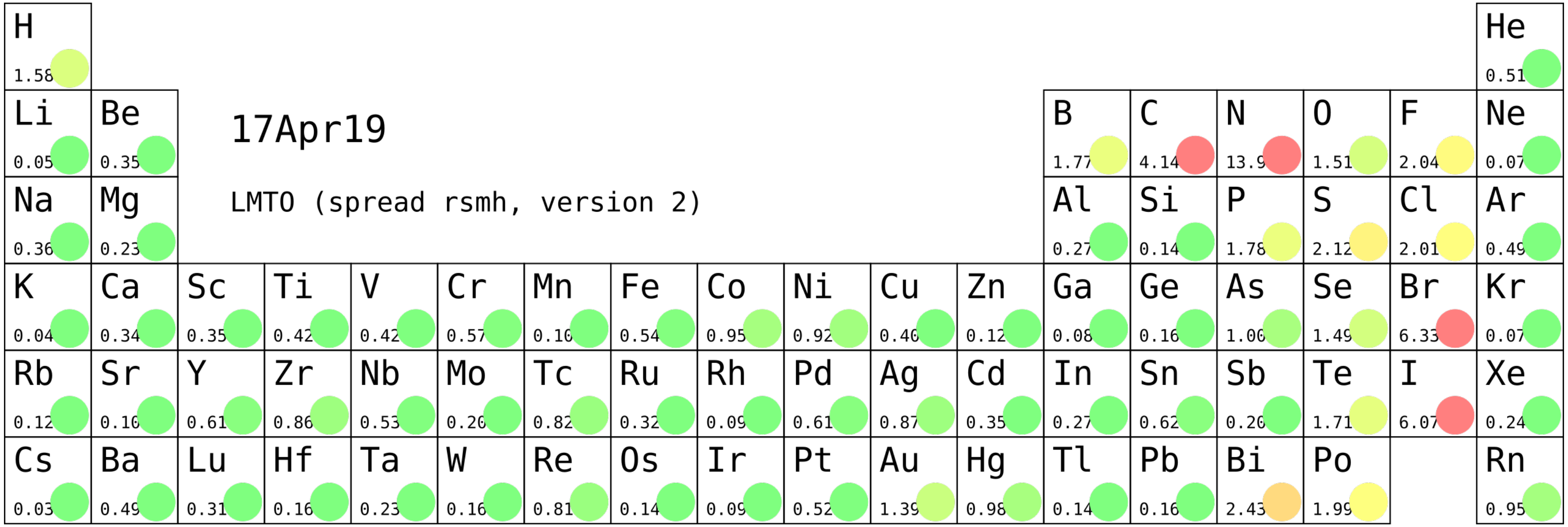


Accessiblity

Make Questaal easily accessible w/ relatively low barriers to use

Goal: competent nonspecialists able to perform routine calculations

- Web site with tutorials
- User interface can be simple or sophisticated
- Input files can be autogenerated (mostly)
- Ticketing system
- Code validation, e.g. Delta Codes project --- similar to best codes

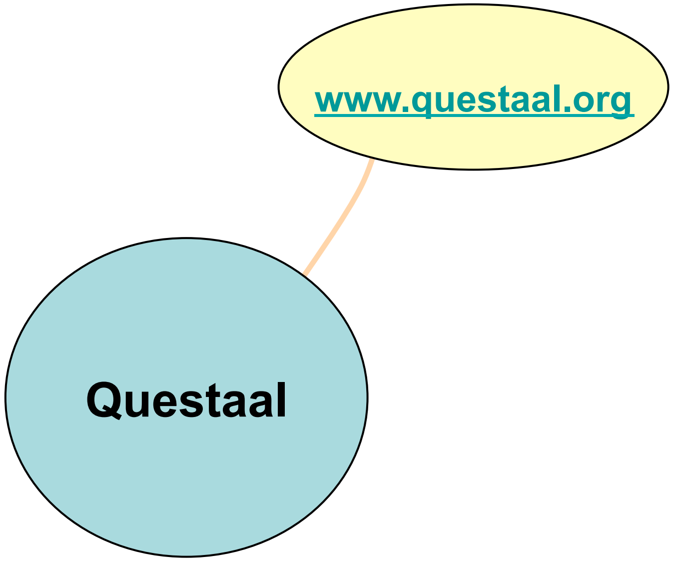


17Apr19

LMTO (spread rsmh, version 2)

H 1.58																	He 0.51
Li 0.05	Be 0.35											B 1.77	C 4.14	N 13.9	O 1.51	F 2.04	Ne 0.07
Na 0.36	Mg 0.23											Al 0.27	Si 0.14	P 1.78	S 2.12	Cl 2.01	Ar 0.49
K 0.04	Ca 0.34	Sc 0.35	Ti 0.42	V 0.42	Cr 0.57	Mn 0.10	Fe 0.54	Co 0.95	Ni 0.92	Cu 0.40	Zn 0.12	Ga 0.08	Ge 0.16	As 1.00	Se 1.49	Br 6.33	Kr 0.07
Rb 0.12	Sr 0.10	Y 0.61	Zr 0.86	Nb 0.53	Mo 0.20	Tc 0.82	Ru 0.32	Rh 0.09	Pd 0.61	Ag 0.87	Cd 0.35	In 0.27	Sn 0.62	Sb 0.20	Te 1.71	I 6.07	Xe 0.24
Cs 0.03	Ba 0.49	Lu 0.31	Hf 0.16	Ta 0.23	W 0.16	Re 0.81	Os 0.14	Ir 0.09	Pt 0.52	Au 1.39	Hg 0.98	Tl 0.14	Pb 0.16	Bi 2.43	Po 1.99		Rn 0.95

Web site



Modern, with many nice features.

- Each main code documented.
- Basic tutorials for functionality
- Mostly complete; still missing links

Web site built on Markdown (Kramdown) system

- Easily extended; intended for user community to add
- There is style manual for uniform look and feel

We hope you will help us identify problems with the web site!
If there are mistakes or you can't find something, let us know.

We welcome contributions to the site (tutorials, new features),
e.g. link to phononpy

Nearly Ultimate Basis: Jigsaw Puzzle Orbitals

Dimitar Pashov

Jerome (next speaker) will show how reasonable envelope parameters can be automatically found. But not optimum!

Idea: construct sophisticated envelope functions that "almost" solve the 1-particle SE without any diagonalization step.

Schrodinger equation $[-\nabla^2 + V(\mathbf{r}) - \varepsilon]\psi$

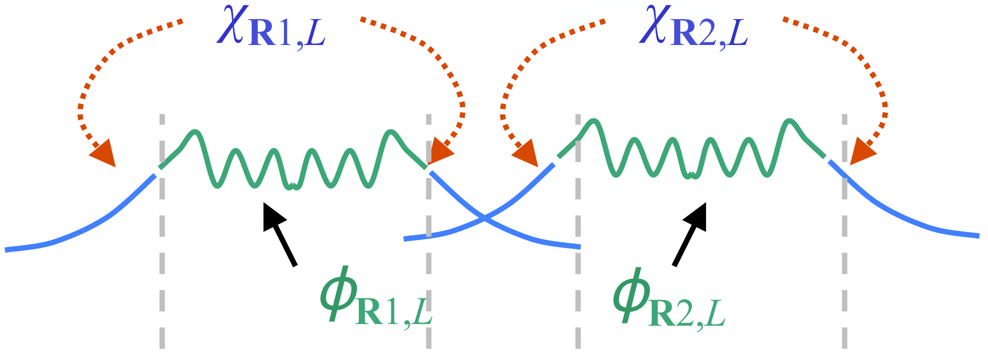
Use properties of Augmented wave basis

⇒ near exact in augmentation spheres

Recall MTO construction

Inside MT, partial waves

$\phi_{\mathbf{R}l}$ is *near exact.*

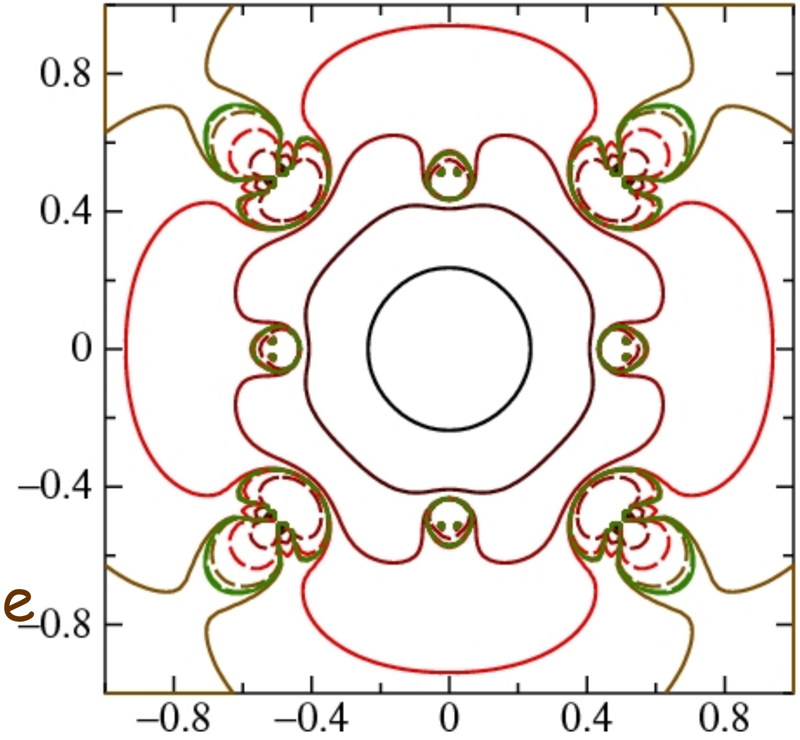


JPO's do something similar but for real potentials

Short-sightedness of JPO's

The JPO's have the following very useful properties:

1. Solves the SE with minimum number of basis functions for a given accuracy in the four dimensions $(\mathbf{r}, E)$
2. Very short ranged
3. Atom centered with a fixed l character



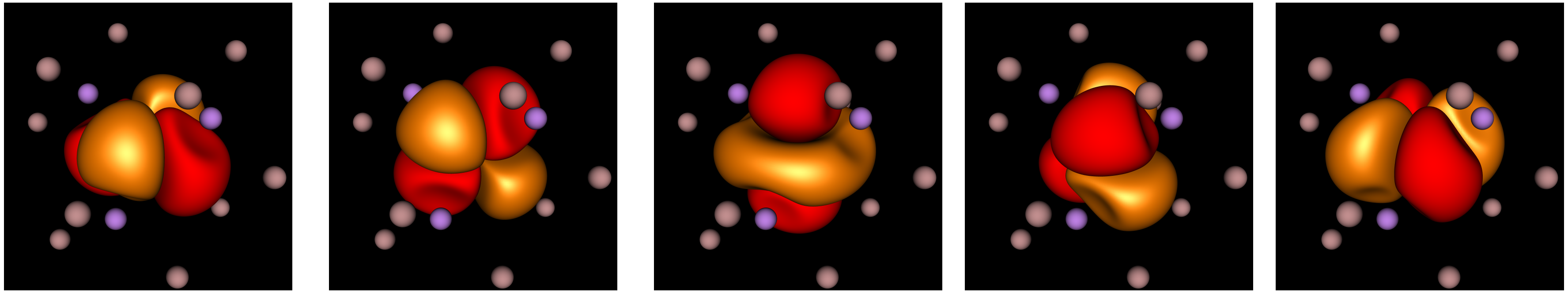
Correlations (other than plasmons) are mostly short ranged. Localized one-particle basis are essential to exploit this physics

Today these are normally Wannier functions or partial waves in augmentation spheres. JPO's will do the job much better.

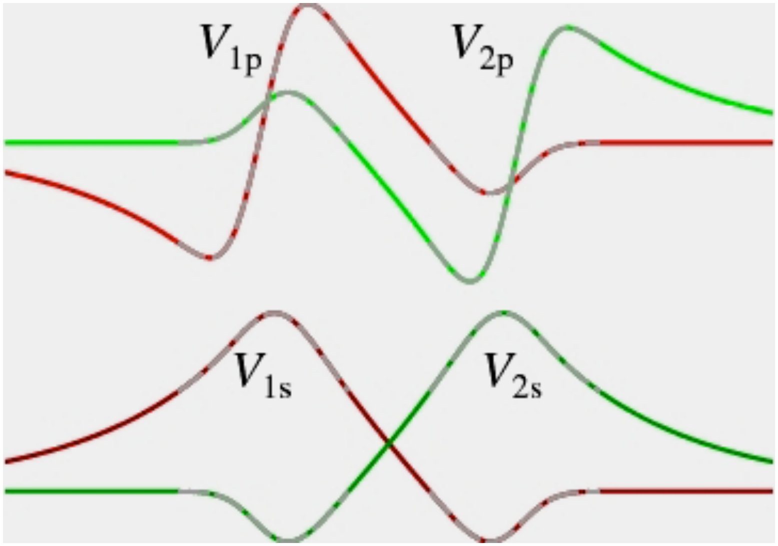
Properties of Jigsaw Puzzle Orbitals

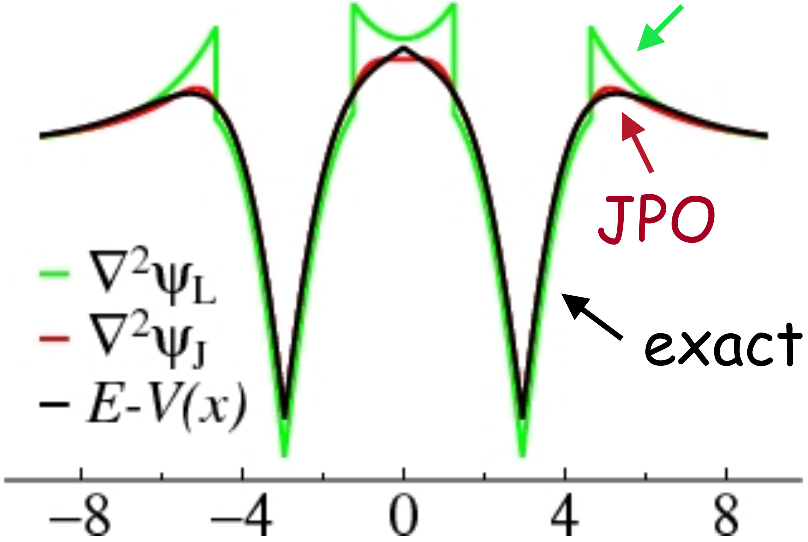
Example : d orbitals in an open zincblende structure

Orbitals are very short ranged with nearly pure $l=2$ character



1D model





LMTO

JPO

exact

Managing Four-Center Integrals in GW

The LDA works with products of basis function pairs, e.g. to make potential matrix elements $\langle \chi_i \,|\, V \,|\chi_j\rangle$ or $n(\mathbf{r})$.

GW and HF are more complicated. They require 4-center integrals with 2 basis functions of $\mathbf{r}$ and two functions of $\mathbf{r}'$ for two-point quantities, e.g. $v_{ijkl} = \langle\, \psi_i\, \psi_j \;|\, 1/|\mathbf{r}-\mathbf{r}'| \;|\, \psi_k\, \psi_l \,\rangle$

Eigenfunction:

$$\psi_{\mathbf{k}n}(\mathbf{r}) = \sum_{Ru} \alpha^{\mathbf{k}n}_{Ru} \Phi^{\mathbf{k}}_{Ru}(\mathbf{r}) + \sum_{\mathbf{G}} \beta^{\mathbf{k}n}_{\mathbf{G}} P^{\mathbf{k}}_{\mathbf{G}}(\mathbf{r}),$$

$$P^{\mathbf{k}}_{\mathbf{G}}(\mathbf{r}) = \begin{cases} 0 & \text{if } \mathbf{r} \in \text{any MT} \\ \exp(i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}) & \text{otherwise} \end{cases}$$

Interstitial :

$$P^{\mathbf{k}_1}_{\mathbf{G}_1}(\mathbf{r}) \times P^{\mathbf{k}_2}_{\mathbf{G}_2}(\mathbf{r}) = P^{\mathbf{k}_1+\mathbf{k}_2}_{\mathbf{G}_1+\mathbf{G}_2}(\mathbf{r}) \qquad e^{-i(\mathbf{k}+\mathbf{G}')\cdot\mathbf{r}} \times e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} = e^{-i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}}$$

Augmentation

$$\Phi_L(\mathbf{r})\Phi_{L'}(\mathbf{r}) = \underbrace{\phi_l(r)\phi_l(r)}_{\text{Numerical solution}} \times \underbrace{Y_{L'}(\hat{\mathbf{r}})Y_{L'}(\hat{\mathbf{r}})}_{\text{Products of } Y_L}$$

$$Y_K(\hat{\mathbf{r}})Y_M(\hat{\mathbf{r}}) = \sum\nolimits_L C_{KLM} Y_L(\hat{\mathbf{r}})$$

Product Basis

Interstitial: use $P_{\mathbf{G}_1}^{\mathbf{k}_1}(\mathbf{r}) \times P_{\mathbf{G}_2}^{\mathbf{k}_2}(\mathbf{r}) = P_{\mathbf{G}_1+\mathbf{G}_2}^{\mathbf{k}_1+\mathbf{k}_2}(\mathbf{r}), \quad P_{\mathbf{G}}^{\mathbf{k}} = e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$

Augmentation: Construct complete set of product functions $B_N(\mathbf{r})$: $\{\varphi_{Ru}(\mathbf{r}) \times \varphi_{Ru'}(\mathbf{r})\}$ spanned by $B_N(\mathbf{r})$

R is a site index; u is a compound index which contains : L, label whether partial wave is $\phi_{\mathbf{R}L}$ or $\partial\phi_{\mathbf{R}L}/\partial E$ or local orbital character.

In practice we must work with Bloch sums $B_I^{(\mathbf{k})}$ of the B_I .

Thus, the mixed basis completely spans the Hilbert space of basis function products $\{M_I^{\mathbf{k}}(\mathbf{r})\} \equiv \{P_{\mathbf{G}}^{\mathbf{k}}(\mathbf{r}), B_{RN}^{\mathbf{k}}(\mathbf{r})\}$

The M_I are not orthogonal so we must orthonormalize

$$|\tilde{M}_I^{\mathbf{k}}\rangle \equiv \sum_{I'} |M_{I'}^{\mathbf{k}}\rangle (O^{\mathbf{k}})_{I'I}^{-1}, \quad O_{I'I}^{\mathbf{k}} = \langle M_{I'}^{\mathbf{k}} | M_I^{\mathbf{k}}\rangle.$$

Input required to make the Self-Energy

The bare coulomb operator can be expanded in the mixed basis:

$$v(\mathbf{r},\mathbf{r}') = \sum_{\mathbf{k},I,J} |\tilde{M}_I^{\mathbf{k}}(\mathbf{r})\rangle v_{IJ}(\mathbf{k}) \langle \tilde{M}_J^{\mathbf{k}}(\mathbf{r}')|$$

Similarly for all 2-point quantities, e.g. the dielectric function ε and screened coulomb interaction $W(\mathbf{r}, \mathbf{r}', \omega)$.

Complete information to generate the GW self-energy :

1. α & β parameterizing eigenfn and eigenvalues

$$\psi_{\mathbf{k}n}(\mathbf{r}) = \sum_{Ru} \alpha_{Ru}^{\mathbf{k}n} \Phi_{Ru}^{\mathbf{k}}(\mathbf{r}) + \sum_{\mathbf{G}} \beta_{\mathbf{G}}^{\mathbf{k}n} P_{\mathbf{G}}^{\mathbf{k}}(\mathbf{r}), \quad \varepsilon_{\mathbf{k}n}$$

2. Matrix elements mapping to the product basis $\langle \Psi_{\mathbf{q}n} | \Psi_{\mathbf{q}-\mathbf{k}n'} M_I^{\mathbf{k}} \rangle$

3. Overlap of the product basis $O_{I'I}^{\mathbf{k}} = \langle M_{I'}^{\mathbf{k}} | M_I^{\mathbf{k}} \rangle$

4. The coulomb matrix $v_{IJ}(\mathbf{k}) \equiv \langle M_I^{\mathbf{k}} | v | M_J^{\mathbf{k}} \rangle$

Augmented part + IPW part

Fock Exchange and RPA polarizability

Matrix elements of Fock exchange integrals in the mixed basis:

$$\langle \Psi_{\mathbf{q}n} | \Sigma_{\mathrm{x}} | \Psi_{\mathbf{q}m} \rangle = -\sum_{\mathbf{k}}^{\mathrm{BZ}} \sum_{n'}^{\mathrm{occ}} \sum_{IJ} \langle \Psi_{\mathbf{q}n} | \Psi_{\mathbf{q}-\mathbf{k}n'} \tilde{M}_I^{\mathbf{k}} \rangle v_{IJ}(\mathbf{k}) \langle \tilde{M}_J^{\mathbf{k}} \Psi_{\mathbf{q}-\mathbf{k}n'} | \Psi_{\mathbf{q}m} \rangle$$

Matrix elements of RPA polarizability

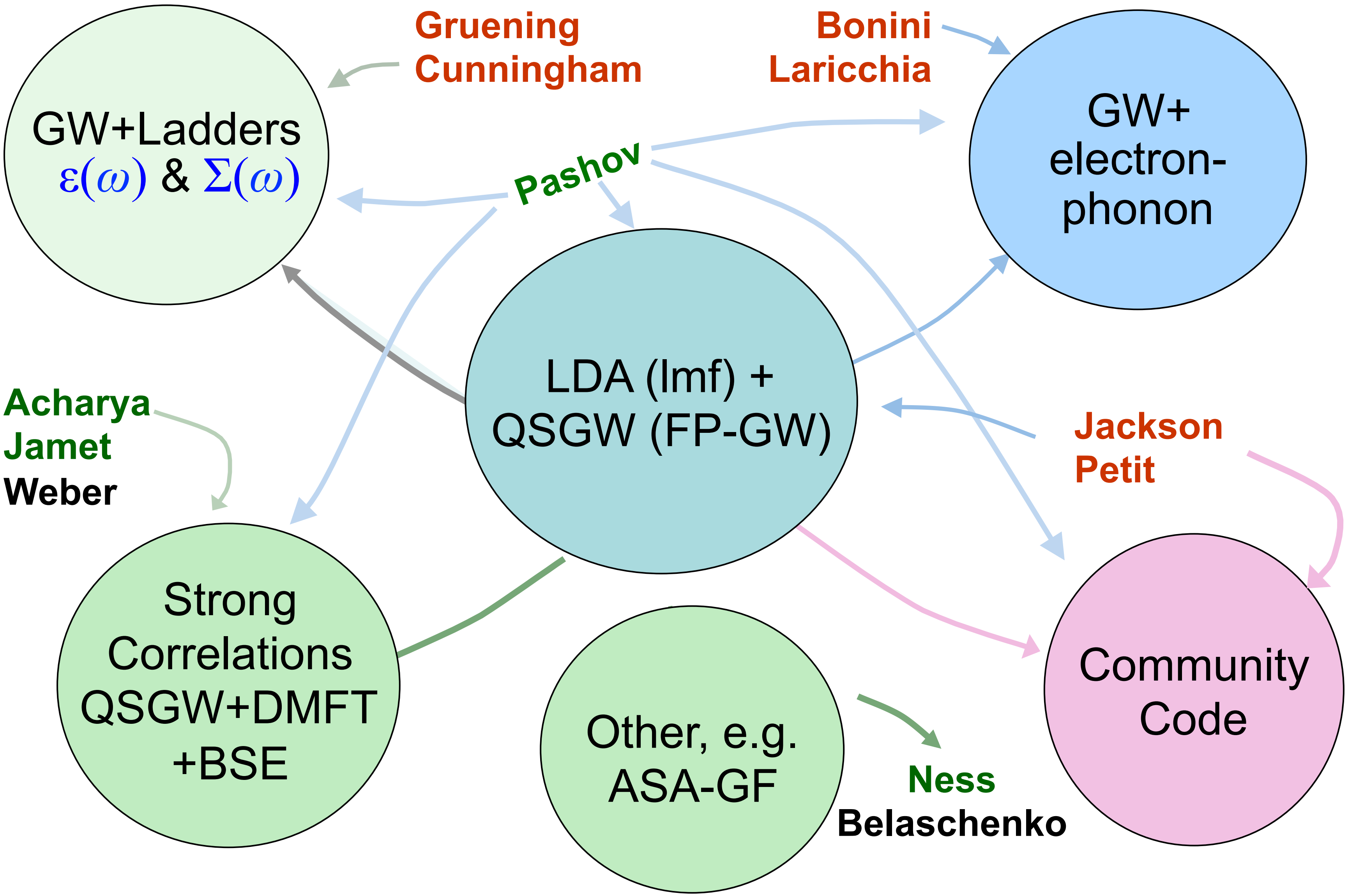
$$P_{IJ}(\mathbf{q},\omega) = \frac{\langle \tilde{M}_I^{\mathbf{q}} \Psi_{\mathbf{k}n} | \Psi_{\mathbf{q}+\mathbf{k}n'} \rangle \langle \Psi_{\mathbf{q}+\mathbf{k}n'} | \Psi_{\mathbf{k}n} \tilde{M}_J^{\mathbf{q}} \rangle}{\omega - (\varepsilon_{\mathbf{q}+\mathbf{k}n'} - \varepsilon_{\mathbf{k}n}) + i\delta} + \frac{\langle \tilde{M}_I^{\mathbf{q}} \Psi_{\mathbf{k}n} | \Psi_{\mathbf{q}+\mathbf{k}n'} \rangle \langle \Psi_{\mathbf{q}+\mathbf{k}n'} | \Psi_{\mathbf{k}n} \tilde{M}_J^{\mathbf{q}} \rangle}{-\omega - (\varepsilon_{\mathbf{k}n} - \varepsilon_{\mathbf{q}+\mathbf{k}n'}) + i\delta}$$

Matrix elements of Screened Coulomb interaction

$$W_{IJ}(\mathbf{q},\omega) = \left\{ v(\mathbf{q})[1 - v(\mathbf{q}) P(\mathbf{q},\omega)]^{-1} \right\}_{IJ}$$

Correlation part of self-energy can be calculated from W_{IJ}.
See Phys. Rev. B76, 165106.

CCP9 Flagship structure



GW+Ladders $\varepsilon(\omega)$ & $\Sigma(\omega)$

Gruening
Cunningham

Bonini
Laricchia

GW+ electron-phonon

Pashov

LDA (lmf) + QSGW (FP-GW)

Acharya
Jamet
Weber

Jackson
Petit

Strong Correlations QSGW+DMFT +BSE

Other, e.g. ASA-GF

Ness
Belaschenko

Community Code