

密度汎関数を超えた 第一原理計算の取り組み

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Contents

- DFT
 - PMT
- Beyond DFT
 - GW*
 - LSMO
 - QMC
 - MnO clusters

First-principles study

Schrödinger eq.
$$H = -\frac{1}{2}\Delta_i + \frac{Z_a}{|r_i - R_a|} + \frac{1}{|r_i - r_j|}$$
 a: atoms, I,j: electrons

Hartree-Fock eq. Assuming $\Psi = |\phi_1 \phi_2 \dots \phi_N|$ $\min \langle \Psi | H | \Psi \rangle$

One body problem
$$\left[-\frac{1}{2}\Delta + \frac{Z_a}{|r - R_a|} + \frac{\langle j | j \rangle}{|r - r_j|} - \frac{|j\rangle\langle j|}{|r - r_j|} \right] |i\rangle = \varepsilon_i |i\rangle$$

Hartree Fock term

$$E = T + E_{nuc} + E_{ee} = T + E_{nuc} + E_H + E_X$$

Correlation energy, E_C

$$E_{tot} = T + E_{nuc} + E_{ee} = T + E_{nuc} + E_H + E_X + E_C$$

Koopmans' theorem

$$\varepsilon_i^N = E_N - E_{N-1} = -I_i$$

$$\varepsilon_{LUMO} = E_{N+1} - E_N$$

Density functional theory (1)

One body problem

$$\Psi = |\phi_1 \phi_2 \dots \phi_N| \left[-\frac{1}{2} \Delta + \frac{Z_a}{|r - R_a|} + \frac{\rho(r_j)}{|r - r_j|} - \frac{|j\rangle\langle j|}{|r - r_j|} + v_C \right] |i\rangle = \varepsilon_i |i\rangle$$

Local density approximation (LDA)

Non local exchange term $-\frac{|j\rangle\langle j|}{|r - r_j|} \rightarrow$ local exchange term $v_X(\rho(r_i))$
(Slater approximation)

from uniform electron gas (HF)

$v_C \rightarrow$ local correlation term $v_C(\rho(r_i))$

from uniform electron gas
(diffusion Monte Carlo)

LDA (Kohn-Sham) Hamiltonian

$$\left[-\frac{1}{2} \Delta + \frac{Z_a}{|r - R_a|} + \frac{\rho(r_j)}{|r - r_j|} + \frac{v_X(\rho(r)) + v_C(\rho(r))}{= v_{XC}(\rho)} \right] |i\rangle = \varepsilon_i |i\rangle$$

Total energy

$$E_{tot}^{LDA} = T + E_{nuc} + E_H + \underbrace{E_X^{LDA} + E_C^{LDA}}_{= E_{XC}^{LDA}}$$

Density Functional Theory (2)

For uniform electron gas (metal)

$$E_{tot}^{exact} = E_{tot}^{LDA} = T + E_{nuc} + E_H + E_{XC}^{LDA}$$

Janak's theorem

$$\frac{\partial E_{tot}}{\partial f_i} = \varepsilon_i \quad \text{Orbital occupancy: } f_i$$

... ε_i , \neq quasiparticle energy

any physical meanings? (later)

Density Functional Theory (3)

Simple, conventionally $O(N^3)$

widely used

$\varepsilon_i \sim$ quasiparticle energy

Success in many cases

Drawbacks: Δ Smaller band gap

Δ $\varepsilon_i \sim$ quasiparticle energy: wider in d, smaller in s,p

X Strongly correlated systems, Mott insulators

X some cases, e.g., van der Waals interaction

Accurate?

Transferability

LDA: $E^{LDA} = E^{exact}$ Exact for uniform electron gas

And expect accurate description for other systems

transferability [uniform electron gas (metal) \rightarrow molecules, crystals]

But LDA or GGA fails in some cases...

Other approaches (hybrid functional): $E \cong E^{exact}$ Exact for a training set

Many forms of E_X and E_C are proposed. E.g., VWN,PBE,LYP,...

$$E_{XC} = \sum_{\alpha} a_{\alpha} E_X^{\alpha} + \sum_{\beta} b_{\beta} E_C^{\beta}$$

transferability [a kind of molecules \rightarrow similar/other molecules]

E.g., B3LYP(general), M06,M08(biological systems),...

Zheng et al., J. Chem Theor. Comput. 5, 808 (2009).

Transferability: OK

Superficially correct potential curves also for van der Waals interactions

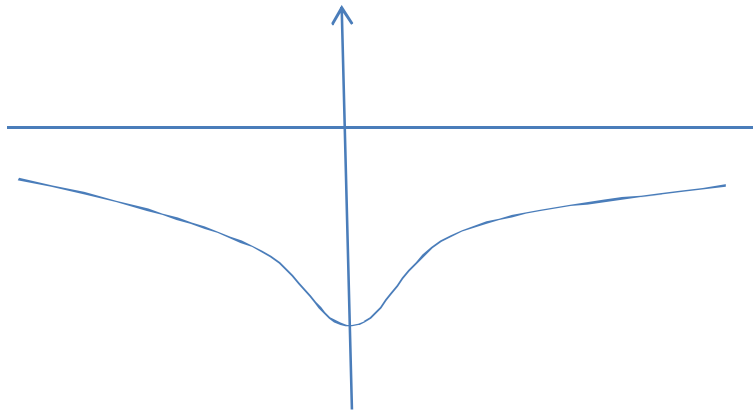
Orbital energy of hybrid functions?

$$\left[-\frac{1}{2}\Delta + \frac{Z_a}{|r - R_a|} + \frac{\rho(r_j)}{|r - r_j|} + v_{XC}^{B3LYP} \right] |i\rangle = \varepsilon_i |i\rangle$$

Orbital energy, ε_i , of hybrid functional \sim quasiparticle energy?

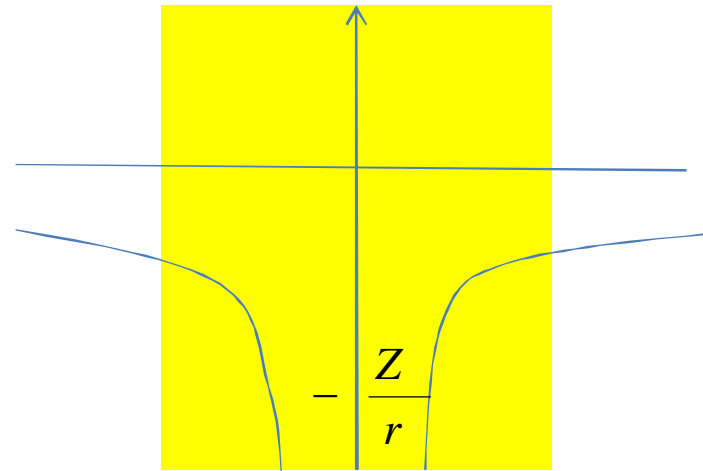
DFT methods

Pseudopotential
(effective core potential)



Potential basis set: Planewave
FFT

All electron



$$|\Psi_n\rangle = |\tilde{\Psi}_n\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{p}_i | \tilde{\Psi}_n \rangle$$

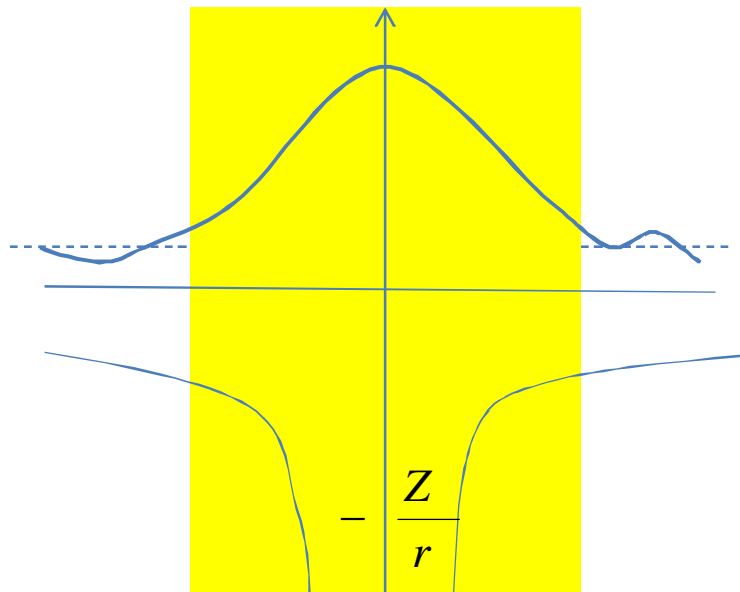
FLAPW: Soler, Williams, PRB40,1560(1989).

PAW: Kresse, PRB 59, 1758 (1999)

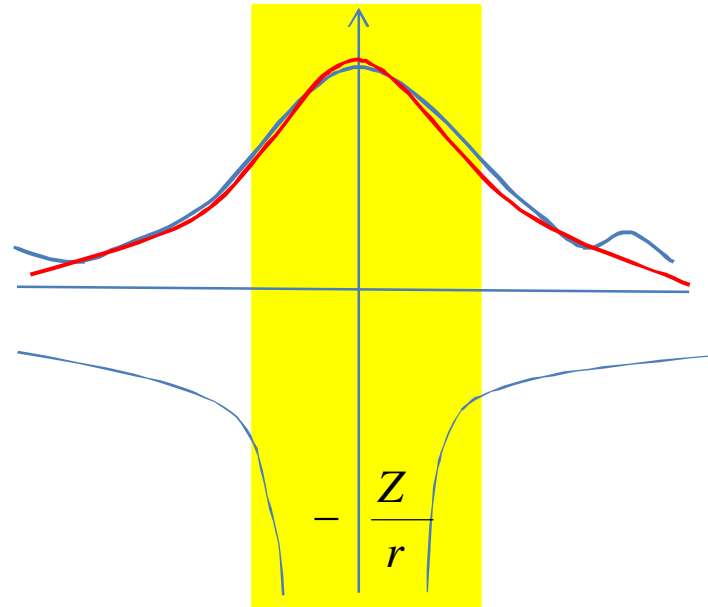
Matrix dimension \uparrow

DFT methods (2), PMT

All electron



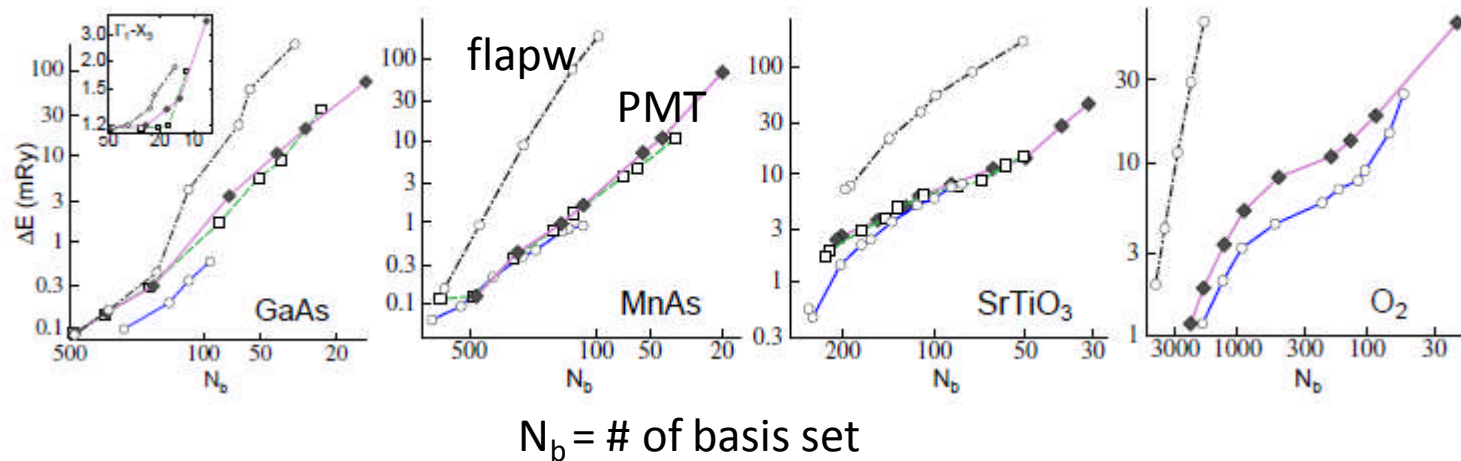
All electron



Smooth tail -> efficient planewave expansion

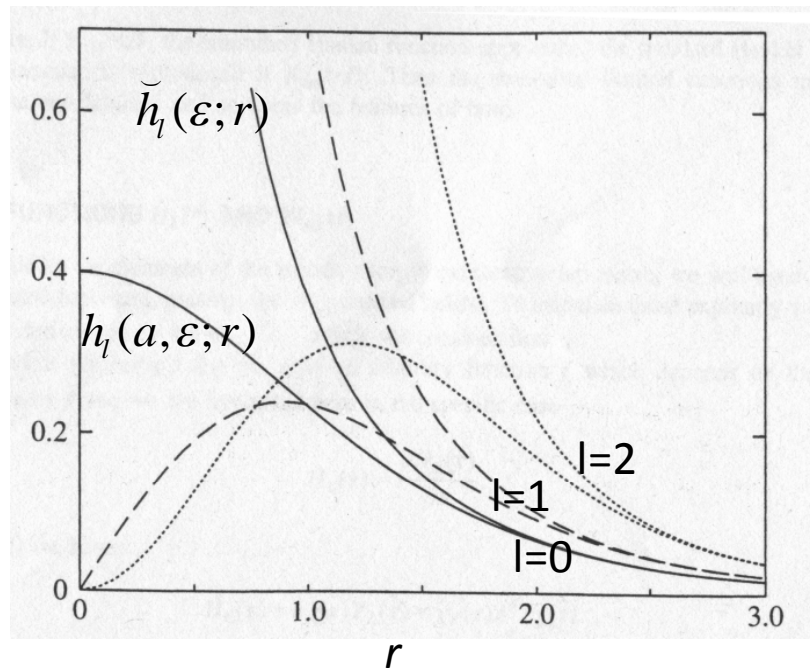
+smoothed Hankel -> efficient expansion

PMT



of PW basis set: \downarrow Crystal: 1/4, Molecules: 1/10)
Computational cost (N^3): crystal: 1/64, Molecules 1/1000

Mathematical footing: Smoothed Hankel function



$$(\Delta + \varepsilon)h_l(a, \varepsilon; r) = -4\pi g_l(a, r)$$

$$g_l(a, r) = C e^{-a^2 r^2} r^l$$

$$h_l(r - R) \sim \sum_l a_{l|l} g_l(r)$$

$$\langle k | h_l(a, \varepsilon) \rangle$$

Search: ecalj

The screenshot shows a Microsoft Internet Explorer browser window with the following details:

- Address Bar:** <http://pmt.sakurane.jp/wiki/index.php?title=EcalJ>
- Search Bar:** Google search for "ecalj".
- Page Title:** EcalJ
- Navigation:** page, discussion, view source, history
- Main Content:**

ecalのホームページです(日本語版)

「ecalパッケージ」には、fullpotential code (fp-lmtoを発展させてPMT法(APW+MTOを混合してつかえる方法)にしたもの)とそれと組み合わせて利用できるself-consistent (あるいはone-shot)GWコードが含まれます。さらには、結晶モデリングツールなども一括して便利に管理できるようにしていきたいと思っています。さらには計算データの共有・蓄積も行っていきたいです。コードの中身と

lm7kは、Mark van Schilfgaarde氏によってとりまとめられたlm-7.0betaのパッケージのうち、full-potential計算の部分とGWドライバー(GW計算との接続部分)を抜き出し、利便性の高いようにすこし手を加えたものです(その改良部分に関しては、鳥取大学小谷岳生、物材機構木野日織が現時点でのおもなcontributorです)。ちょっとしたバグとりと改良を加えています。基本的にはlm-7.0betaの結果を再現します。このバージョンにはPMT(Plane wave and Muffin-tin orbital)法が組み込まれています。PMT法は、MTO基底とAPW基底を同時に使う線形化法です。これにより、「非常に簡単な入力で計算できる(従来のようにMTOのセットアップをする必要がない;結晶構造だけでもかなりの計算ができそれをリファインしていく形で精度のよい解もえられる)」、また安定性、高速性も他の方法(PAW,LAPWなど)に比べて基本的に勝っている(はず)です。ですが、まだまだ実際的には至らないところいろいろとあります(なんとかみなでよってたかってよいものにしていきたいと考えています。ほかのコードではできないようなことや機能を付けかわえていかないといけないし、使いがらでもよくしていかないとけない。協力をお願いします(インストールやテストは現状でも相当にかんたんにごできるよう工夫されてます)。

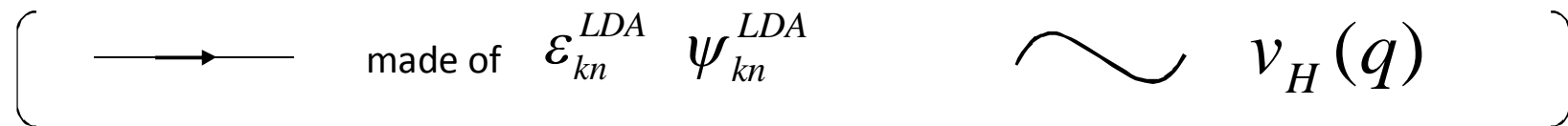
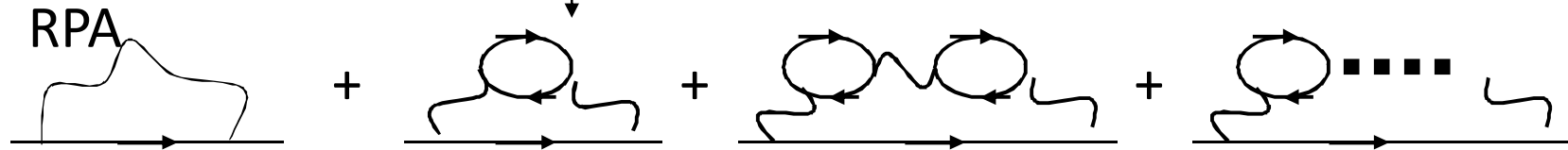
いまや、電子状態計算は、工学的な考え方をとりいれて研究を展開していくべき段階にもなってきています。しかしながら、現状の標準的手法ではまだまだその能力は限定的であり、方法論的にまだまだこれから発展させていくべきところが山積です。将来的には、たとえば電子相関などの問題でいうなら、「磁気揺らぎ交換による電子間引力+電子間のスクリーン相互作用+フォノンの影響、などをフルにとりこんだ高温超電導体の計算」なども可能になると思っていますが、まだまだ基礎技術開発をしっかりとって組み合わせていかないと信頼性ある結果は得られないと思っています(定性的な結果ならモデルで十分立ったりするし、むしろそれの方が役に立つただ「どう定性的に理解するのか(モデルを組み立てるべきか?)」にも電子状態計算は重要な役割を果たします)。

旧バージョンユーザーへ:Enu(占有状態の重心位置)のバグを固定したので、IDMODを使わなくても安定した収束がはかれるようになったようです。ctrlファイルの書き方がすこし変わりましたが、これはlm67 siなどとすることでどこをなせばいいか指摘してくれます。
- Navigation Sidebar:**
 - Set \$wgLogo to the URL path to your own logo image.
 - navigation
 - Main Page
 - Community portal
 - Current events
 - Recent changes
 - Random page
 - Help
 - search
 - Go
 - Search
 - toolbox
 - What links here
 - Related changes
 - Special pages
 - Printable version
 - Permanent link
- Footer:** ページが表示されました

GW

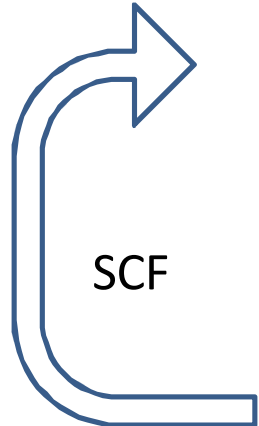
$$\text{LDA} \left[-\frac{\Delta}{2} + v_{nuc} + \int dr' \frac{n(r')}{|r-r'|} + v_{XC}^{LDA}(n(r)) \right] \psi_{kn}^{LDA} = \epsilon_{kn}^{LDA} \psi_{kn}^{LDA}$$

$$\text{GW} \quad \epsilon_{kn}^{LDA} + \left\langle kn' \left| \Sigma(\epsilon_{kn}^{GW}) - v_{XC}^{LDA} \right| kn \right\rangle \rightarrow \epsilon_{kn}^{GW}$$



Comment: based on DFT, Coulomb interaction $U_{nn} \neq U_{n\uparrow n\downarrow}$

QSGW



SCF

$$\left[-\frac{\Delta}{2} + v_{nuc} + \int dr' \frac{n(r')}{|r-r'|} + v_{XC}^{(i)}(n(r)) \right] \psi_{kn}^{(i)} = \epsilon_{kn}^{(i)} \psi_{kn}^{(i)}$$

$$\epsilon_{kn}^{(i)} + \langle kn' | \Sigma^{(i)}(\epsilon_{kn}^{(i+1)}) - v_{XC}^{(i)} | kn \rangle \rightarrow \epsilon_{kn}^{(i+1)}$$

$$\Sigma^{(i)}(\omega) \rightarrow v_{XC}^{(i+1)}$$

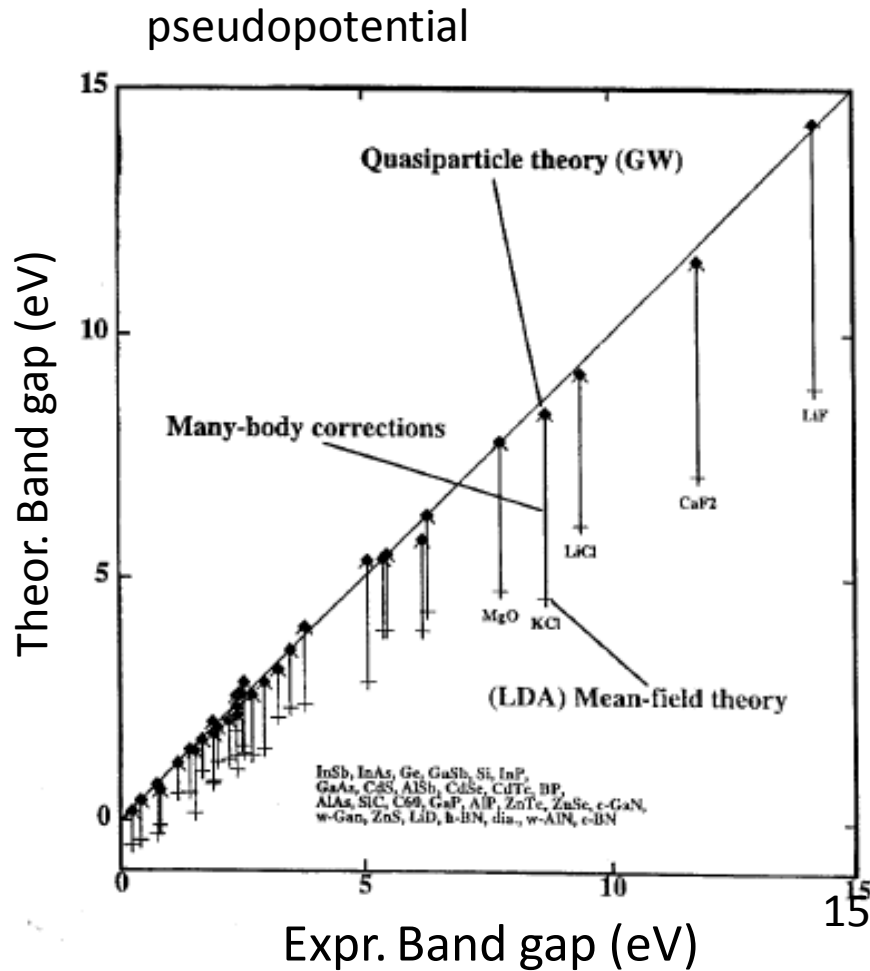
(Ignore imaginary part during SCF)

$$\Delta V(\omega) = H(\omega) - H^0$$

$$\text{Min. } M[V^{\text{eff}}] = \text{Tr}[\Delta V \delta(\omega - H^0) \{\Delta V\}^\dagger] \\ + \text{Tr}[\{\Delta V\}^\dagger \delta(\omega - H^0) \Delta V]$$

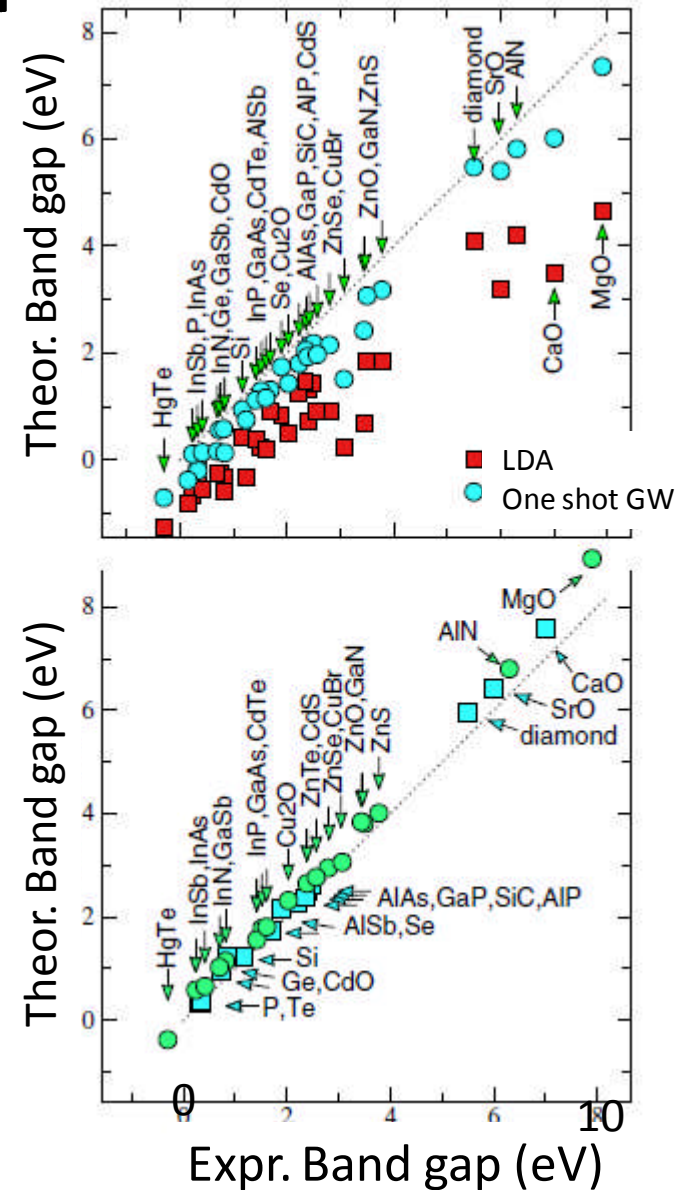
Schilfgaarde et al., PRL96, 226402 (2006).

Band gap



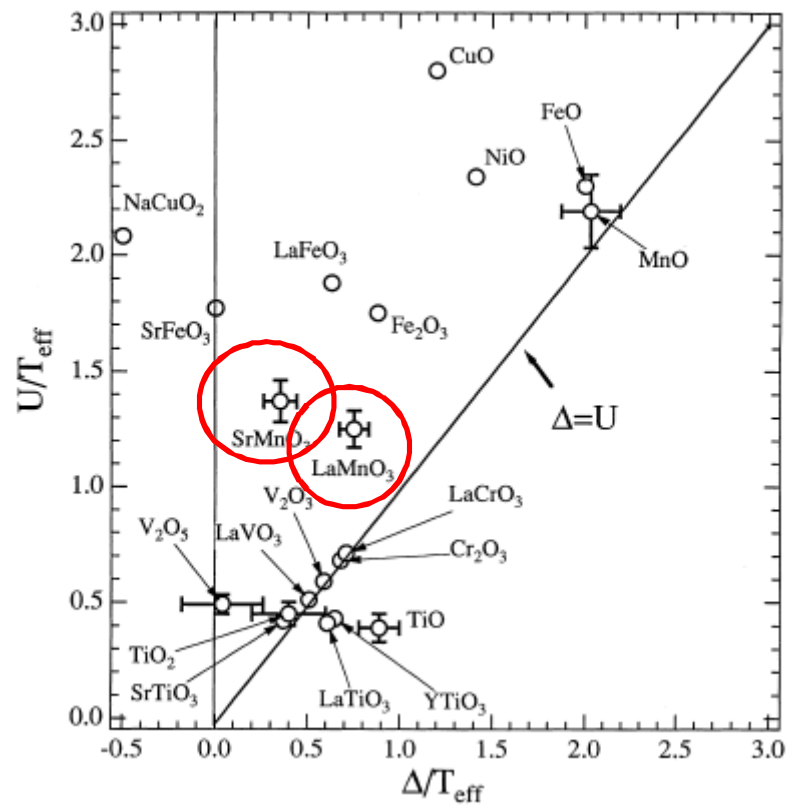
Hedin, J. Phys. Condens. Matter 11, R489 (1999).

All electron



Schilfgaard et al., PRL96, 226402 (2006).

SrMO₃ and LaMnO₃



$\Delta < U$
Charge transfer type

Fig. 1. Zaanen-Sawatzky-Allen U - Δ plot for transition-metal oxides including Ti and V oxides, deduced from cluster-model analyses of the transition-metal 2p core level photoemission spectra [3]. Here, U_{eff} and Δ_{eff} are "effective" U and Δ in which multiplet effects of the d ions are incorporated, and T_{eff} is an effective p-d transfer integral which takes into account the d orbital degeneracy.

Fujimori et al., J. Electron Spec. Related phenom. 117-118, 277 (2001).

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3 = \text{LSMO}$

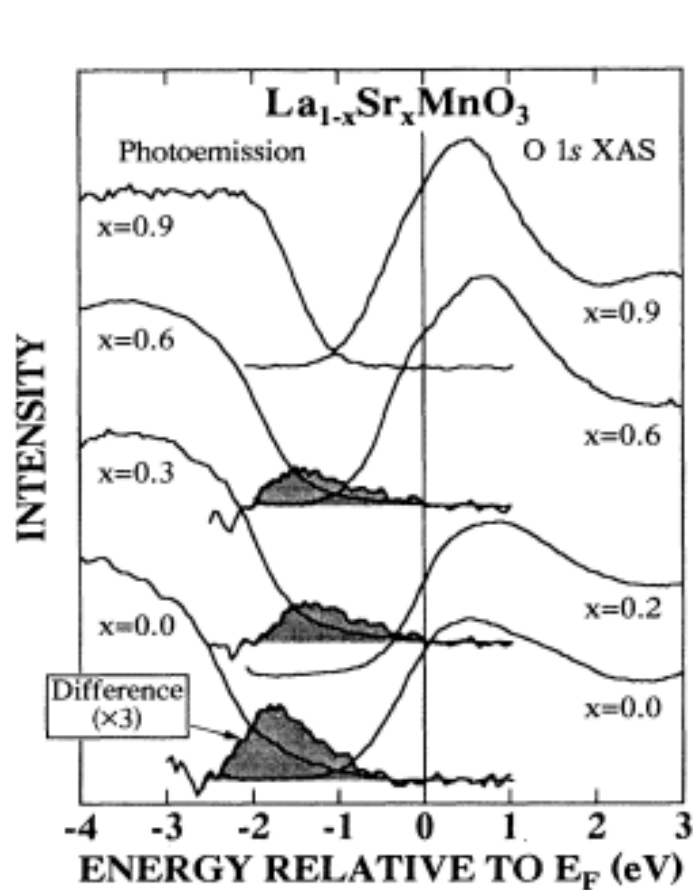
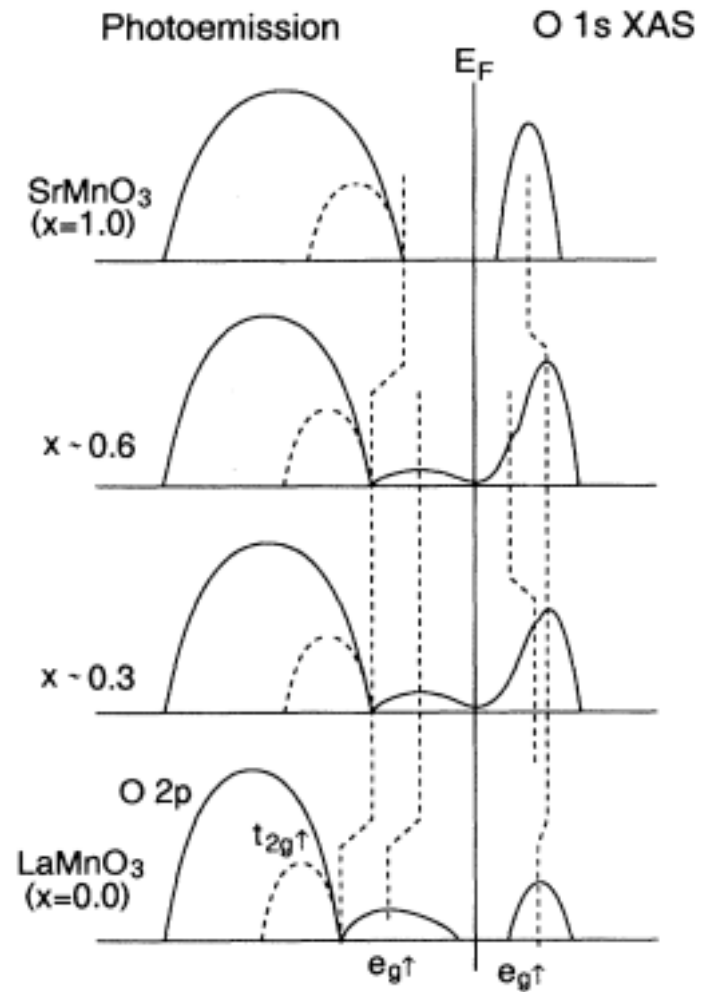


FIG. 11. UPS and O 1s XAS spectra near the Fermi level. The O 1s XAS spectra are references to the O 1s binding energies. The difference spectra relative to $x=0.9$ are also shown. Starting from SrMnO_3 , the intensity of the $e_g\uparrow$ emission in the UPS spectra gradually increases with decreasing x .



Saitoh et al., PRB 51, 13942 (1995).



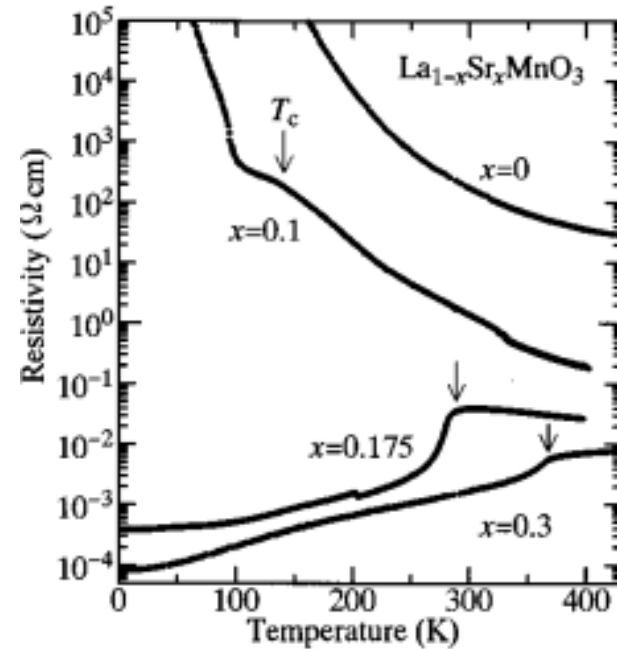
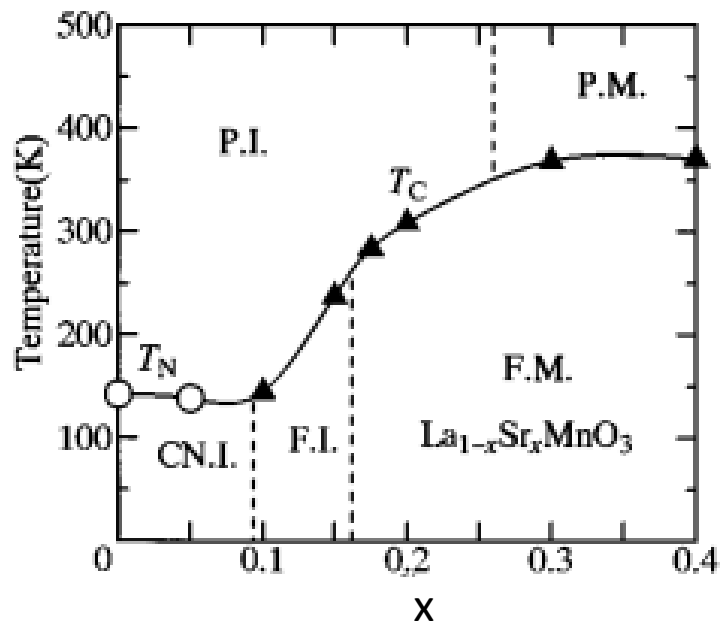
Strongly correlated systems

~ near charge transfer type Mott insulator

Why DFT?

good description of phase diagram, spin wave

Expr. phase diagram



$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \sim \text{La}_{1-x}\text{Ca}_x\text{MnO}_3$

Okimoto et al., PRB 55, 4206 (1997).

Summary of XPS, ARPES and ...

LDA, GGA: Mn 3d, not good

LDA+U: good

unoccup. Mn3d ↑, occup Mn3d ↓

LSMO

LDA, GW DOS

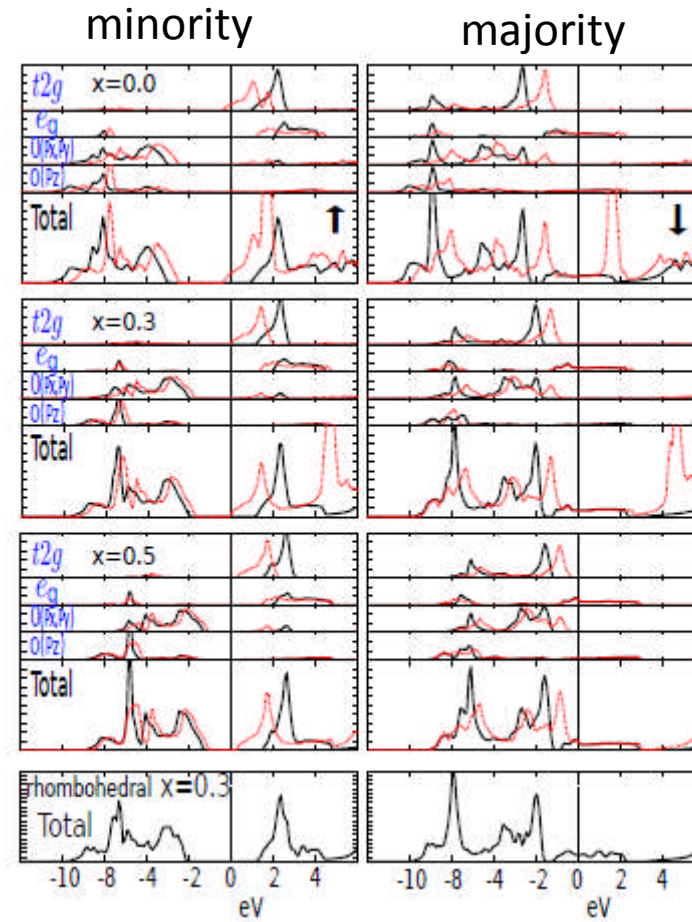
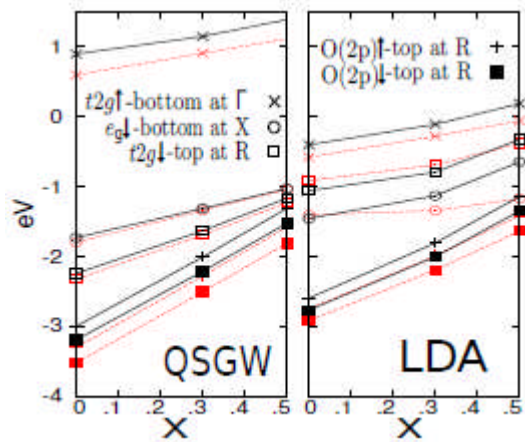
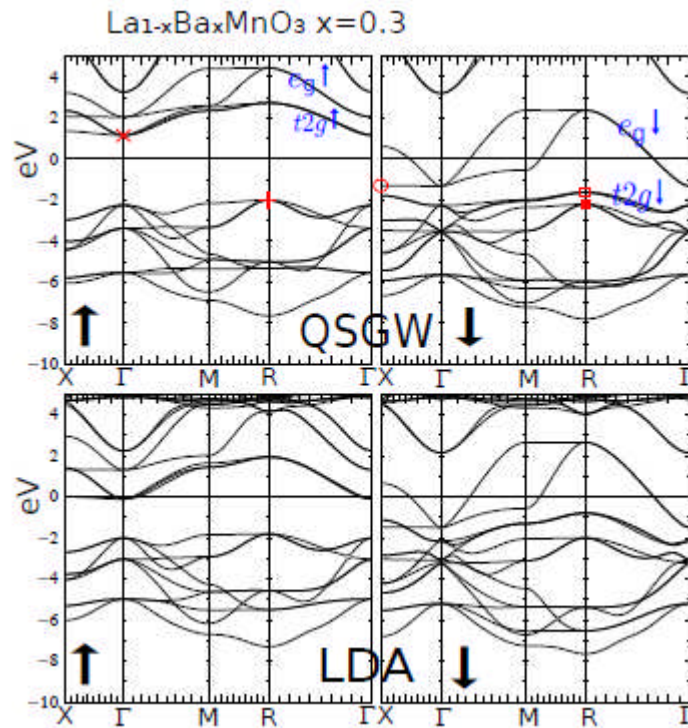


FIG. 2: (color online) Density of states in QSGW (black solid line) and LDA (red dotted line) for $a=3.934\text{\AA}$. 4f band in QSGW is above the plotted region here in QSGW.

FM Spin wave (expr.)

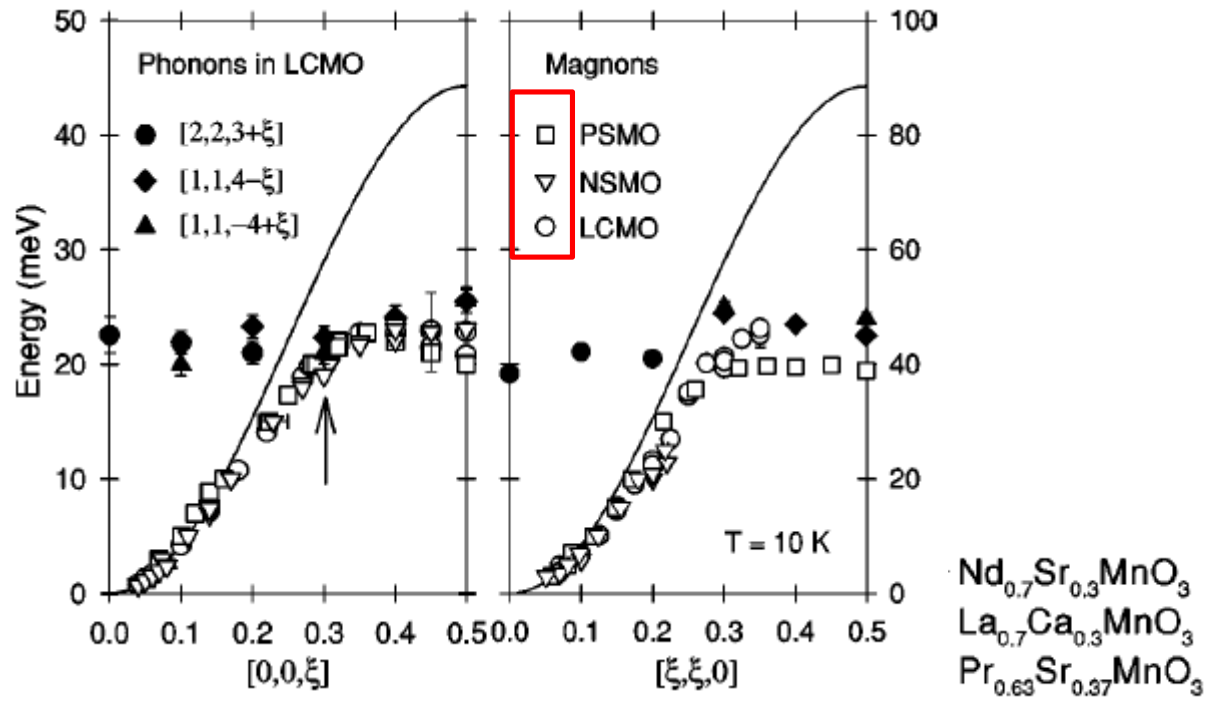
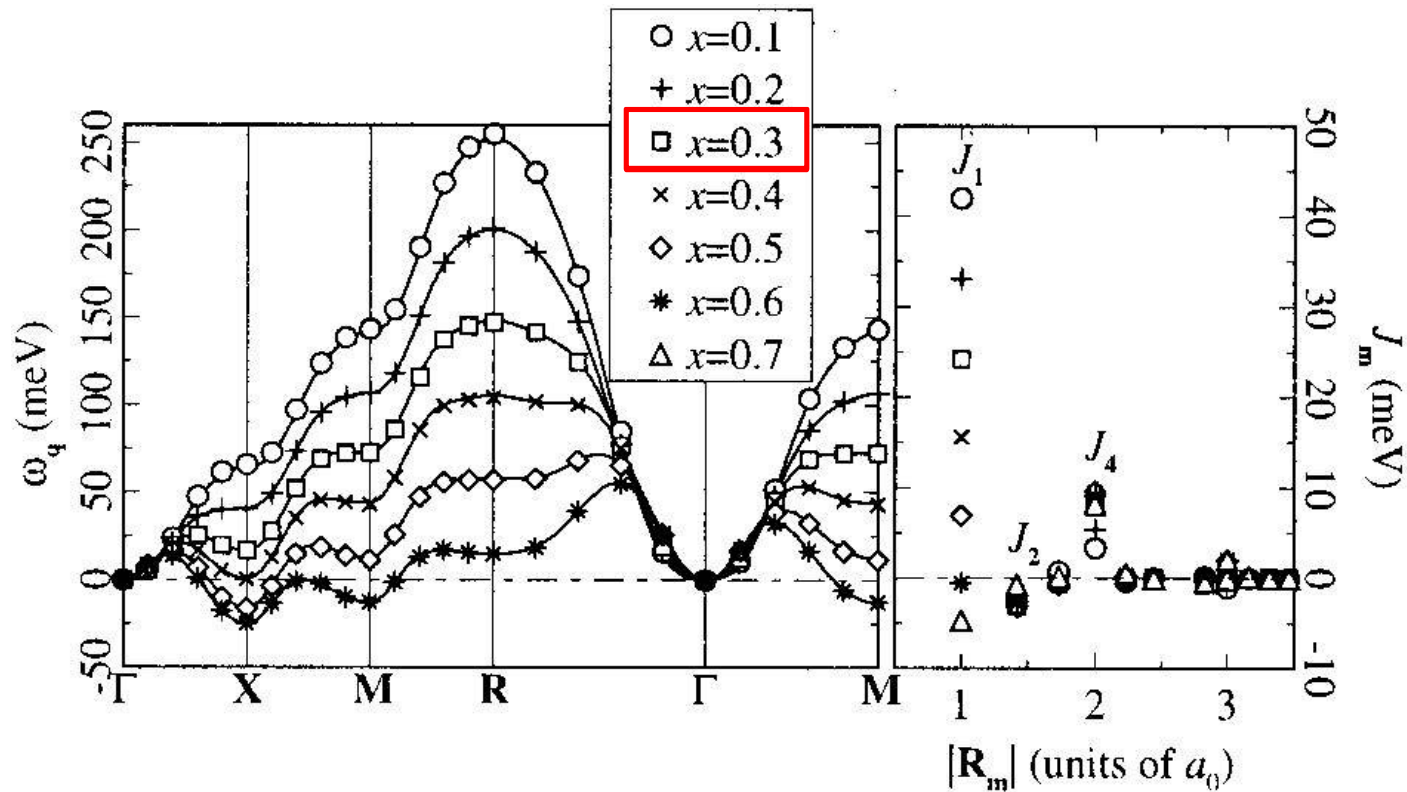


FIG. 2. Open symbols show magnon dispersions along the $[0,0,\xi]$ and $[\xi,\xi,0]$ directions for $\sim 30\%$ manganites PSMO (open squares), LCMO (open circles), and NSMO (open down triangles) at 10 K. The data for PSMO are from Ref. 13. The solid line is a fit to a nearest-neighbor Hamiltonian assuming isotropic spin waves for $\xi < 0.1$. Full symbols show selected LO phonon modes collected along the reciprocal-lattice directions as specified in the legend. The rapid decrease of the manganese magnetic form factor at these large wave vectors ensure that the scattering stem mostly from the lattice vibrations (phonons).

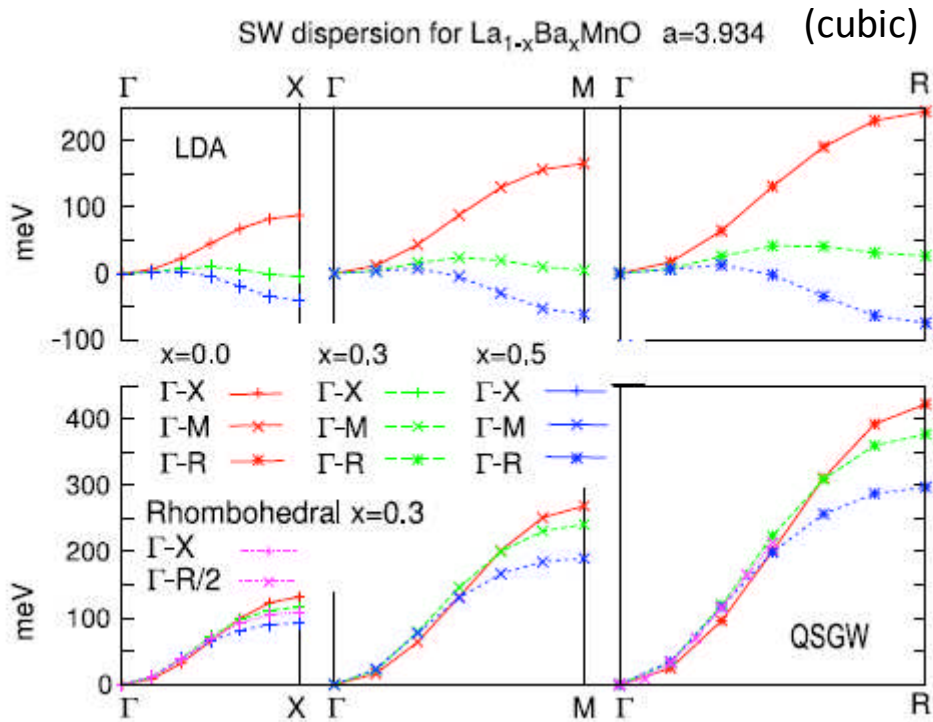
FM Spin wave (LDA,theory)



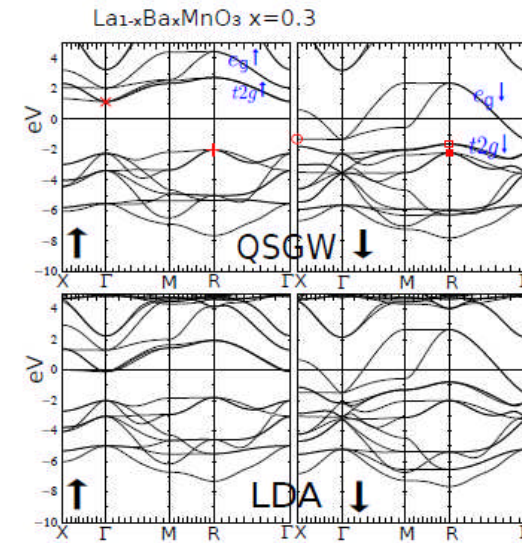
Solovyev and Terakura, ed. Singh and Papaconstantopoulos, "Electronic Structure and Magnetism of Complex Materials", Springer

FM Spinwave (LDA vs GW)

LDA



GW



GW:

larger energy scale ($> \times 2$)

no zone boundary softening

Figure 4. Spin-wave dispersion along Γ -X, Γ -M and Γ -R lines for $a = 3.934$ Å. Negative energy means the unstable modes. We also superpose the spin-wave dispersion in a rhombohedral case for $x = 0.3$ by pink lines (only Γ -X and Γ -R/2 in the QSGW panels). It is almost in the cubic case, where $R/2 = (0.25, 0.25, 0.25)$ in the cubic structure is on the BZ boundary of the rhombohedral structure.

Problems of DFT, *GW*

Strongly correlated systems

Van der Waals - DFT

...

Accuracy?

model potential

~onebody approximation

compare with expr.

Correlated wavefunction

Many body wavefunction

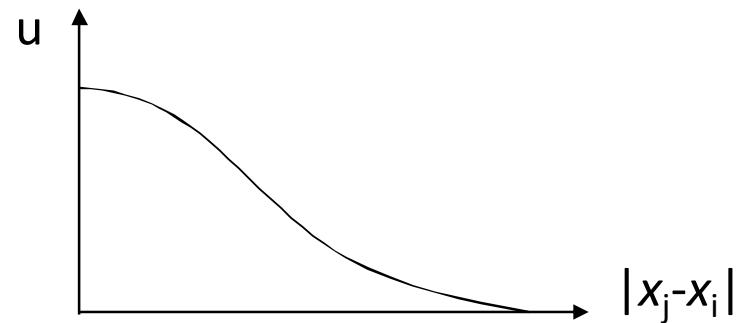
$$\Psi(X) = D_i^\uparrow(R) D_i^\downarrow(R)$$

How to improve?

$$\Psi_T(X) = e^{J(X)} D_i^\uparrow(R) D_i^\downarrow(R)$$

$J(X)$: Jastrow factor

$$J(\mathbf{X}) = \sum_{i=1}^N \chi(\mathbf{x}_i) - \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ (j \neq i)}}^N u(\mathbf{x}_i, \mathbf{x}_j).$$



Ground state of Hamiltonian

$$\begin{aligned} & \lim_{\tau \rightarrow \infty} \langle \mathbf{R} | \exp[-\tau(\hat{H} - E_T)] | \Phi_{\text{init}} \rangle \\ &= \lim_{\tau \rightarrow \infty} \int G(\mathbf{R} \leftarrow \mathbf{R}', \tau) \Phi_{\text{init}}(\mathbf{R}') d\mathbf{R}' \\ &= \lim_{\tau \rightarrow \infty} \sum_l \Psi_l(\mathbf{R}) \exp[-\tau(E_l - E_T)] \langle \Psi_l | \Phi_{\text{init}} \rangle \\ &= \lim_{\tau \rightarrow \infty} \Psi_0(\mathbf{R}) \exp[-\tau(E_0 - E_T)] \langle \Psi_0 | \Phi_{\text{init}} \rangle. \end{aligned}$$

Monte Carlo algorithm

Imaginary time Schrödinger equation ($it \rightarrow t$)

$$-\partial_t \Phi(\mathbf{R}, t) = (\hat{H} - E_T) \Phi(\mathbf{R}, t)$$

→ diffusion Monte Carlo

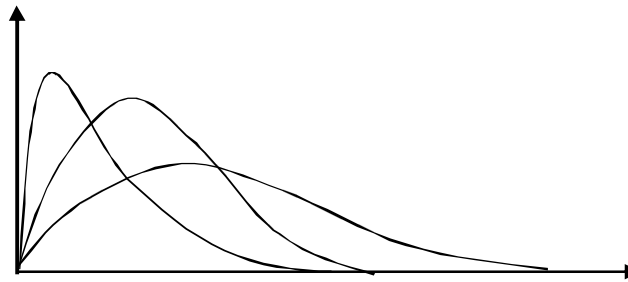
Diffusion Monte Carlo (DMC)

CCSD(T):

basis set dependence

$$N^5, N^6$$

Finite number of basis set

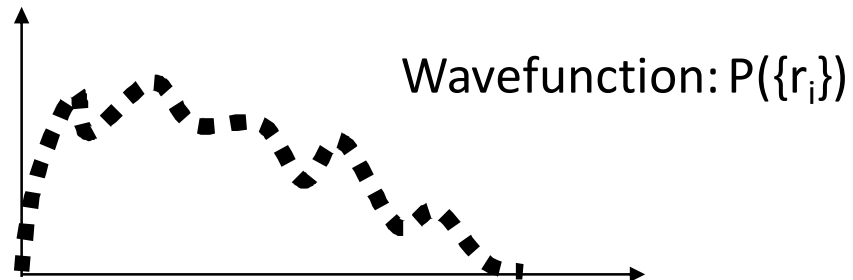


DMC:

no basis set dependence

$$N^{3.5}$$

Infinite number of basis set



$$E_{xc} > 90\%$$

Diffusion Monte Carlo (2)

Accurate

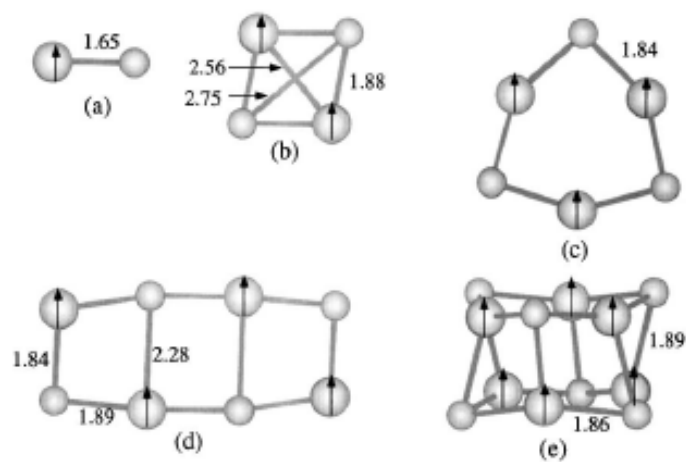
no expr.

But

x1000 (computation time)

$(\text{MnO})_n$ clusters

Becke exchange+PW91 correlation

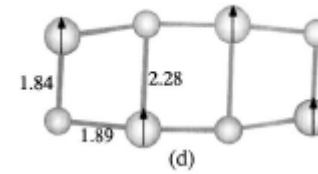


Assuming ferro

Nayak, Jena, PRL 81, 2970 (1998).
JACS 121,644 (1999).

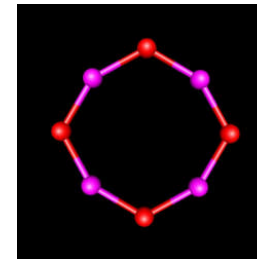
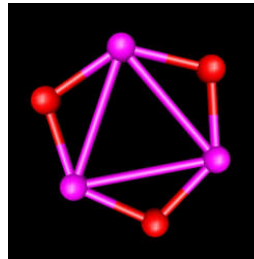
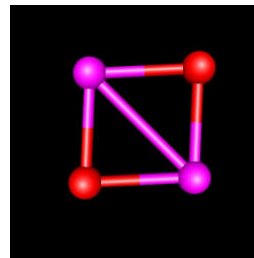
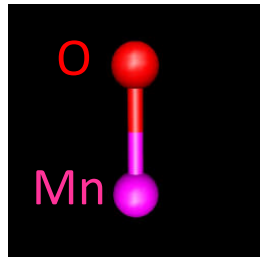
$(\text{MnO})_n$ cluster: result, $n \leq 4$

Assuming ferromagnetic spin alignment



(New structure)

ground state



LSDA,PBE $2S_z+1=6$

9

14

19

B3LYP,DMC $2S_z+1=6$

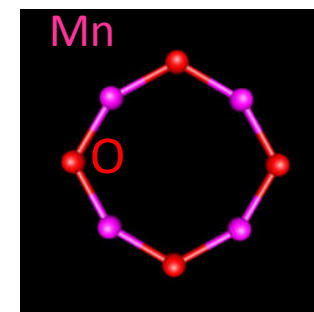
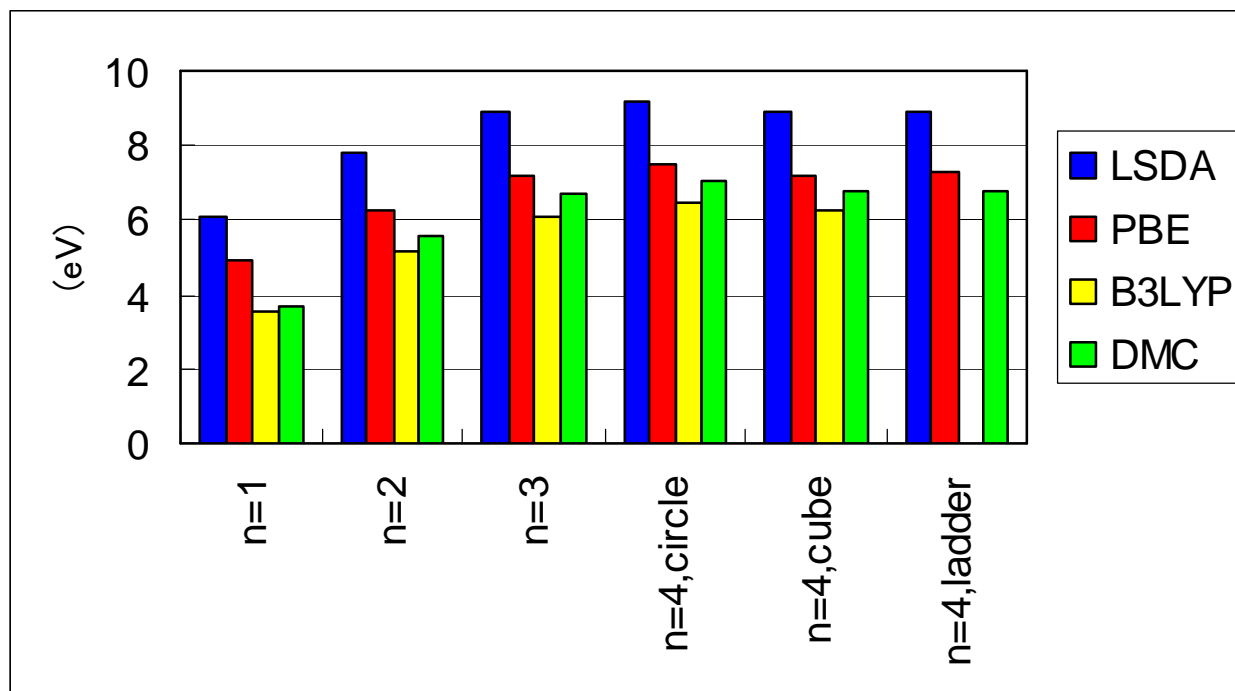
11

16

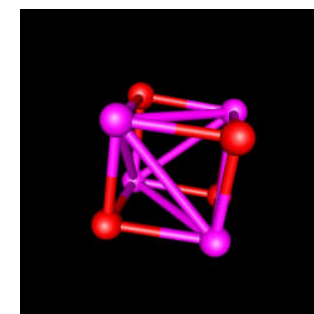
21

(MnO)_n: Binding energy

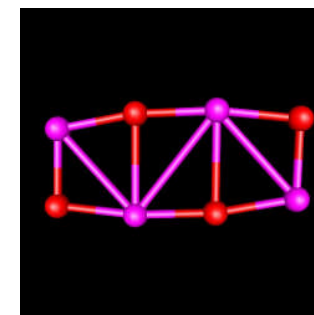
Theoretical binding energies per n



circle



cube



ladder

DMC: B3LYP structure

Atomization energy: LSDA >> PBE > DMC > B3LYP

Spin moment: wrong in LSDA and PBE

First-principles theories

DFT: powerful
but correctness?

