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When magnetism is the driving force of order in alloys…

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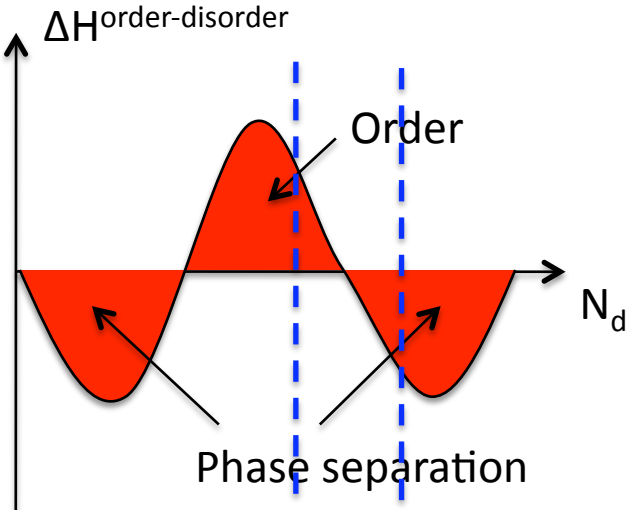
State of the Art…

- FePd, CoRh, CoPt nanoalloys...
  - Can the size of the nanoparticle have an impact on the ordering of the nanoalloy ?

- For CoPt…
  - Is magnetism a major player in order-disorder transitions?
  - If yes, how can it be implemented in a simple inter-atomic potential ?

Magnetism and order…

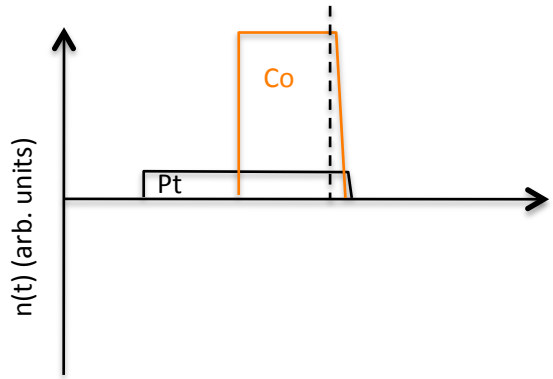
1. In the case of 50:50 alloys of late transition metals …

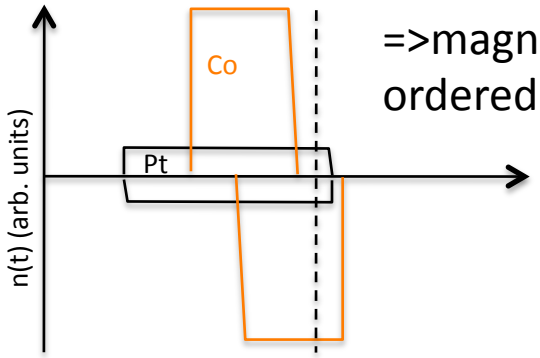


Gautier, Bieber, Ducastelle, …

$$\begin{cases} N_d < 7 \Rightarrow order \\ N_d > 7 \Rightarrow phase\ separation \end{cases}$$

2. Magnetism….





E_f is shifted => N_d is reduced
=>Predicted state is an ordered alloy
=>magnetism produces an ordered state for $Co_{1-x}Pt_x$

Goals…

- Understanding the relationship between order and magnetism:
  - Non magnetic versus magnetic calculations
    - $E_{tot}(V)$
    - Magnetic moment μ
    - Bulk Modulus B
    - Band structure
    - DOS
    - LDOS
- Understanding size and magnetic effects on order.
  - Fourth moment tight binding scheme with (?) magnetism.
    - Fits based on first principle results.
  - Surface/ interface effects.
  - The nanoparticle (cluster).

1. Co and Pt in the elemental bulk form **ab initio**

Ab initio conditions

- ABINIT Code
  - LDA and GGA
  - Norm Conserving Pseudopotentials (Trouiller-Martin) and PAW
- Monkhorst Pack Grid
  - 16x16x16 for Co
  - 20x20x20 for Pt
- Kinetic energy cut off:
  - Co : 16 Ha
  - Pt : 22 Ha
- Full optimization of cell geometry in structure relaxation:
  - Broyden-Fletcher-Coldberg-Shanon (BFCS)
- Cold smearing method of Marzari:
  - Pt: 0.007 Ha
  - Co: 0.010 Ha

PAW GGA versus LDA

- Due to the misrepresentation of the exchange correlation hole, the lattice parameter is underestimated in LDA and overestimated in GGA.

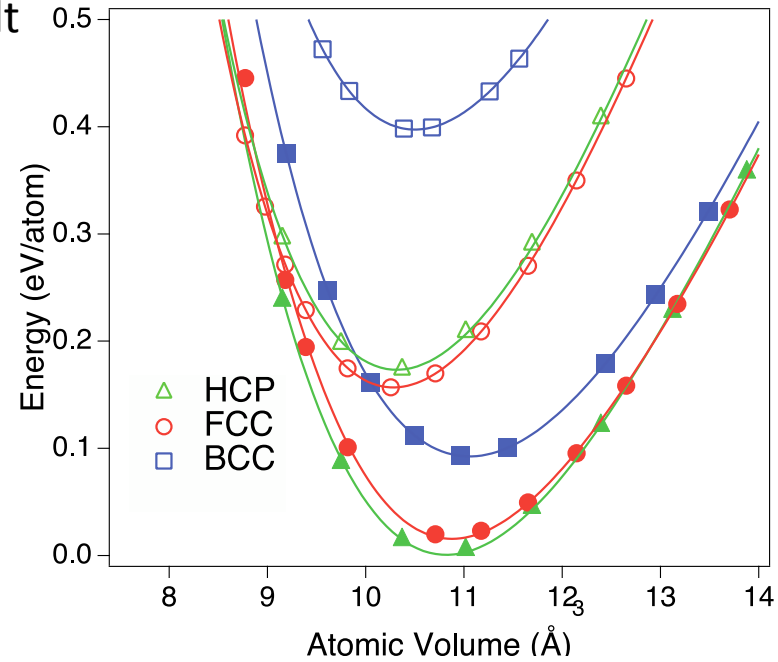
FCC	V_0^{PAW}(Å)	μ_0^{PAW} (μ_B)
Co (LDA)	9.93 (10.0[1], *10.43*[3])	1.54 (*1.61*[4])
Co (GGA)	10.83 (10.90[1], *10.43*[3])	1.64 (*1.61*[4])
Pt (LDA)	14.79 (14.78[2],*15.05*[3])	0
Pt (GGA)	15.65 (15.65[2], 15.05[3])	0

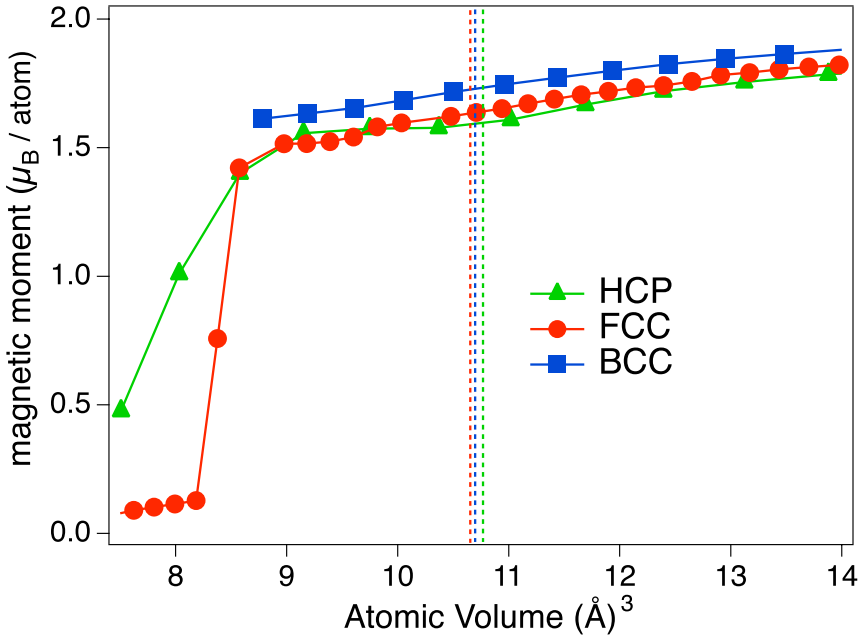
1 Cerny et al.
2 abinit.org
3 Kittel
4 J. Crangle et al.

-Pt is better represented in LDA.
-Co is better in GGA
-Magnetism in Co is better in GGA, this is what interests us… so we choose GGA…

Bulk properties in PAW GGA

Cobalt





Platinum

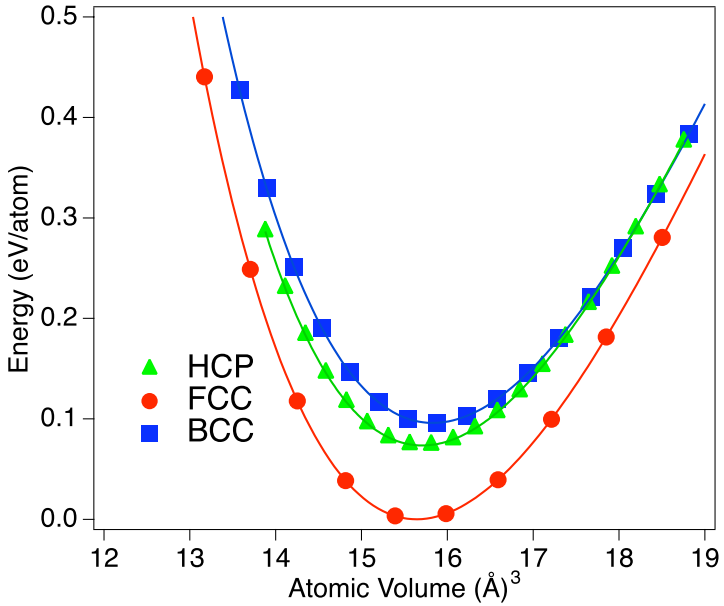


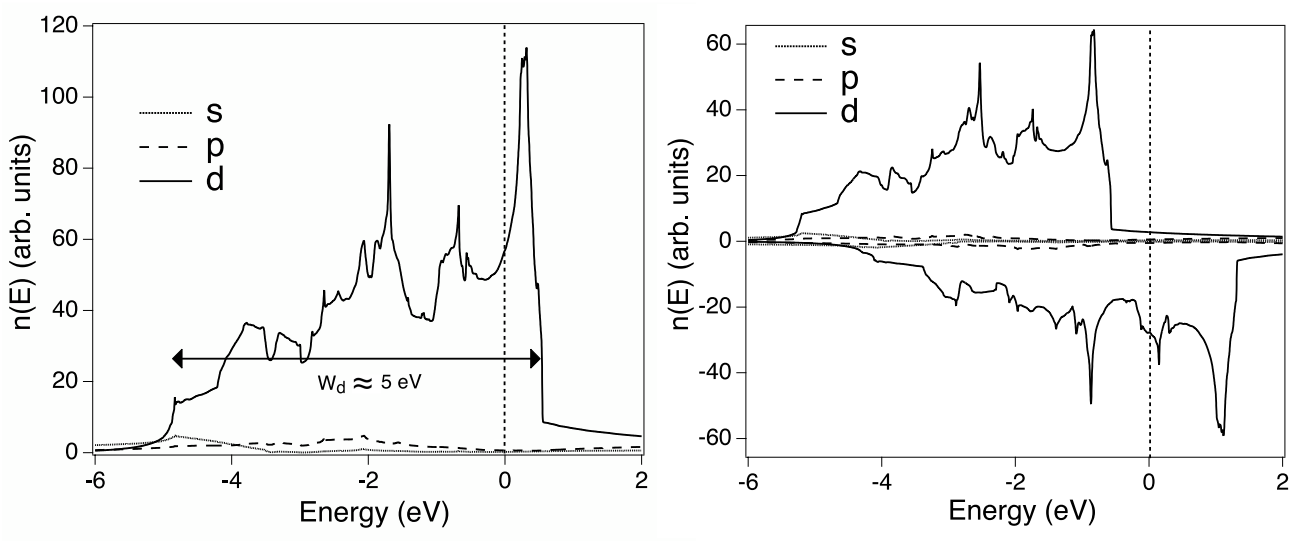
TABLE I: Ground state properties of bulk Co and Pt.

	Phase	V (Å^3)	E (eV/atom)	μ (μ_B)	B (GPa)
Co	hcp (FM)	10.8	0.00	1.60	
	hcp (NM)	10.3	0.17	-	
	hcp (exp)	11.09[6]	0.17	-	
	fcc (FM)	10.8	0.01	1.64	186
	fcc (NM)	10.3	0.16	-	139
	fcc (exp)	11.18[6]	0.16	-	190.5[2]
	bcc (FM)	11.0	0.09	1.75	
	bcc (NM)	10.5	0.40	-	
	bcc (exp)	-	0.40	-	
Pt	hcp (FM)	15.3	0.08	0	
	hcp (NM)	15.3	0.08	0	
	hcp (exp)				
	fcc (FM)	15.7	0.00	0	227
	fcc (NM)	15.7	0.00	0	229
	fcc (exp)				
	bcc (FM)	15.8	0.10	0	
	bcc (NM)	15.8	0.10	0	
	bcc (exp)				

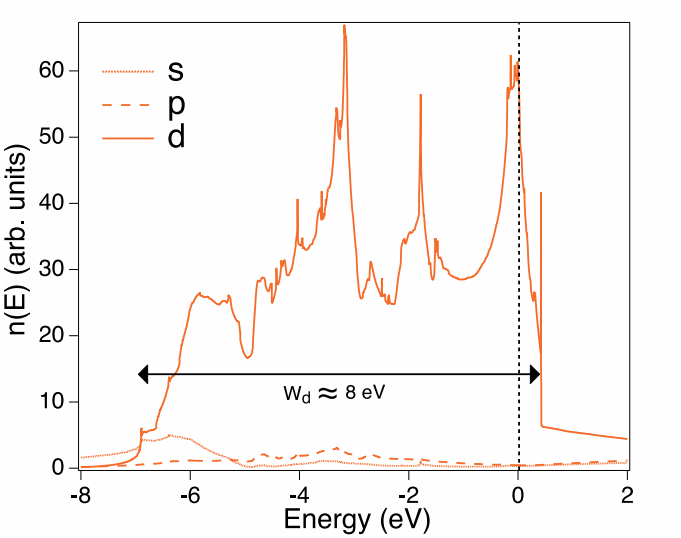
Experimental values from Cerny (2003)

Co and Pt in elemental bulk form …

Co FCC

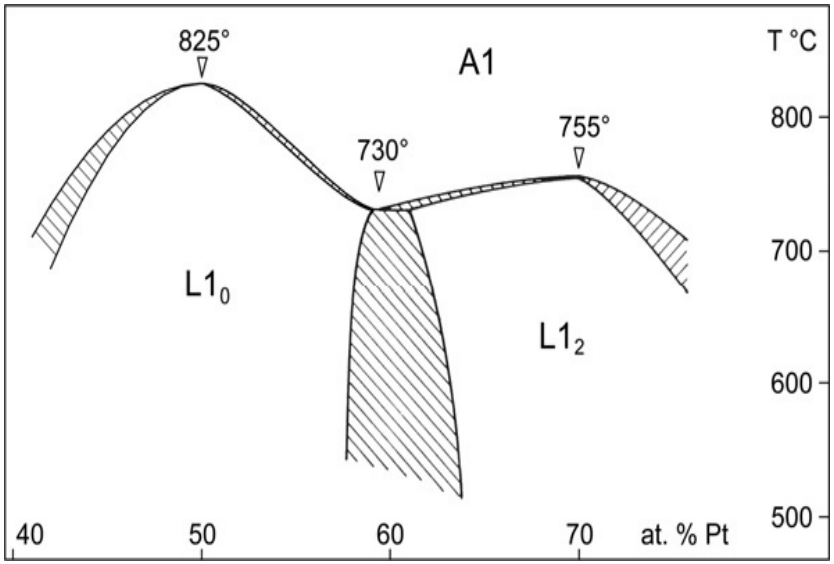


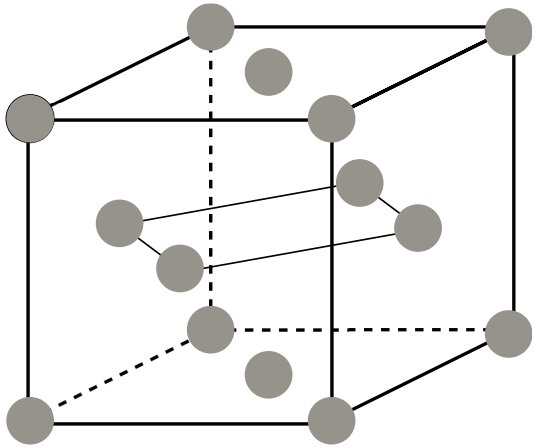
Pt FCC



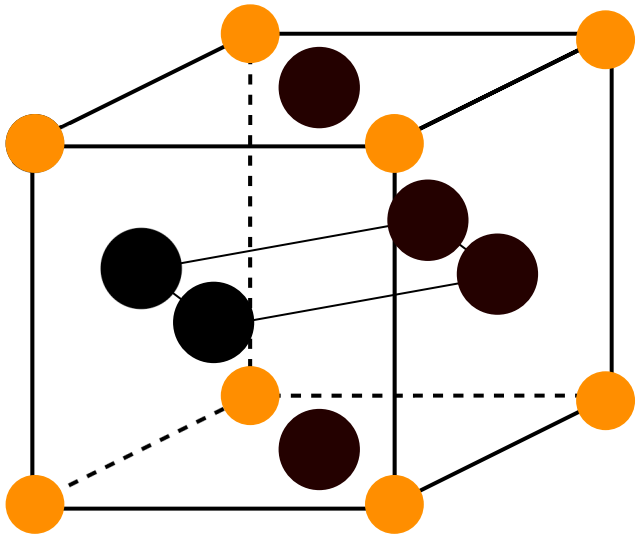
1. Co and Pt in the elemental bulk form
   - LDA versus GGA
2. $Co_{1-x}Pt_x$ in the alloyed bulk form:
   - GGA calculations in the PAW approximation.

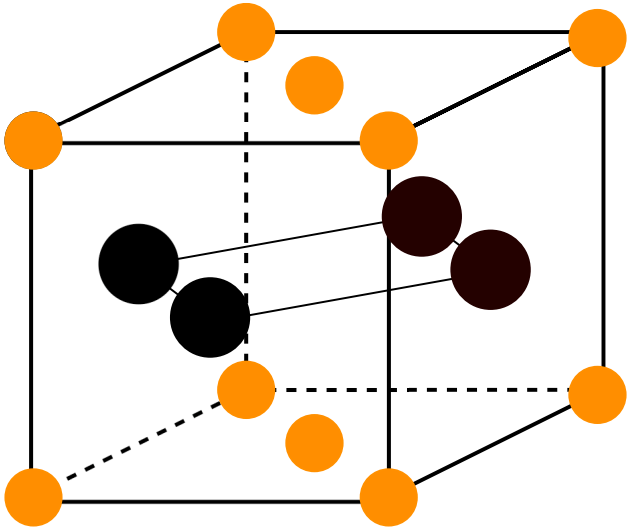
$Co_{1-x}Pt_x$ in the Bulk form…

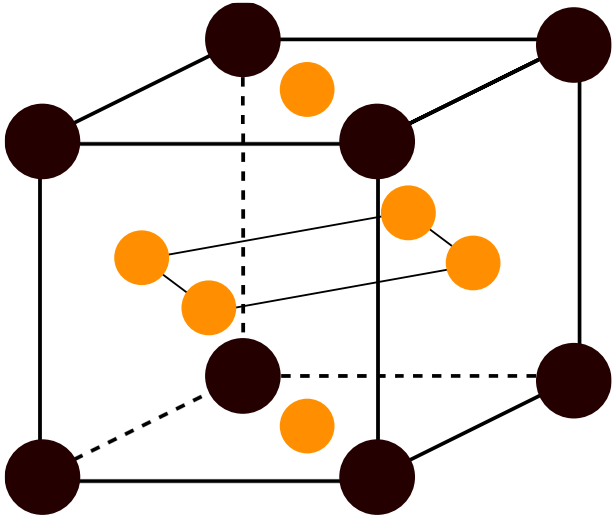




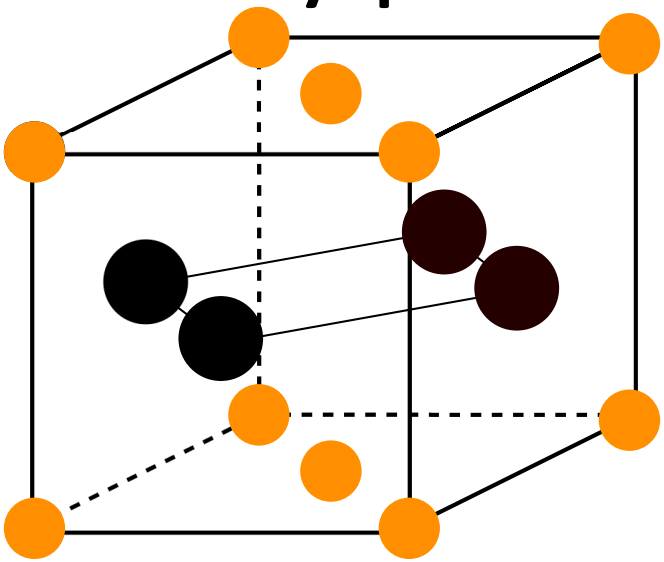
Leroux *et al.*



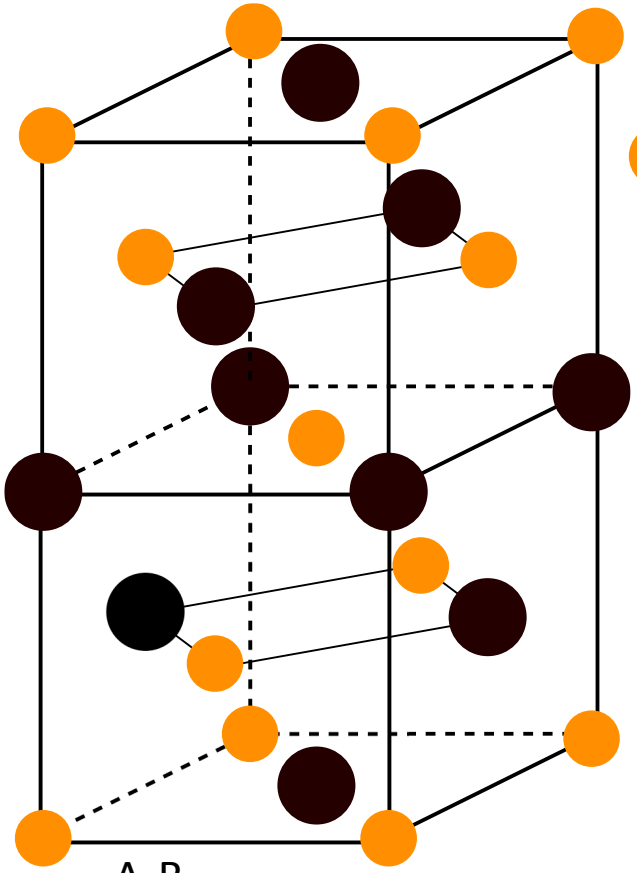




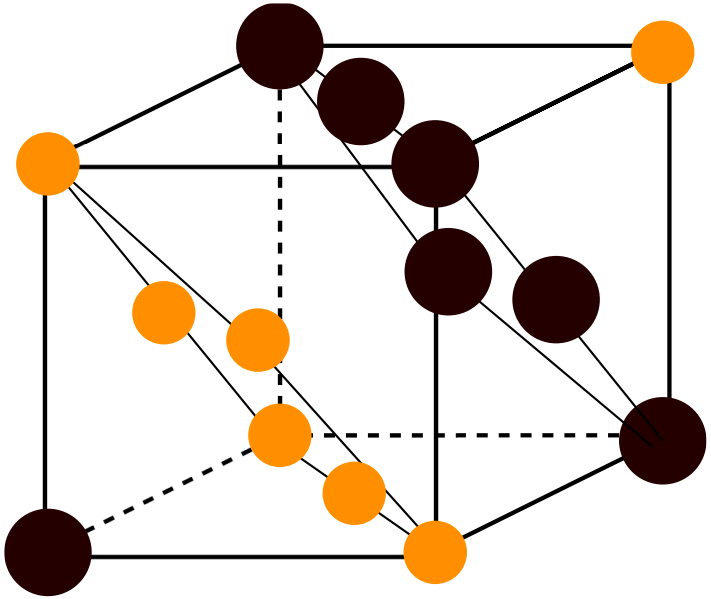
50:50 alloy phases…



$L1_0$



A_2B_2



$L1_1$

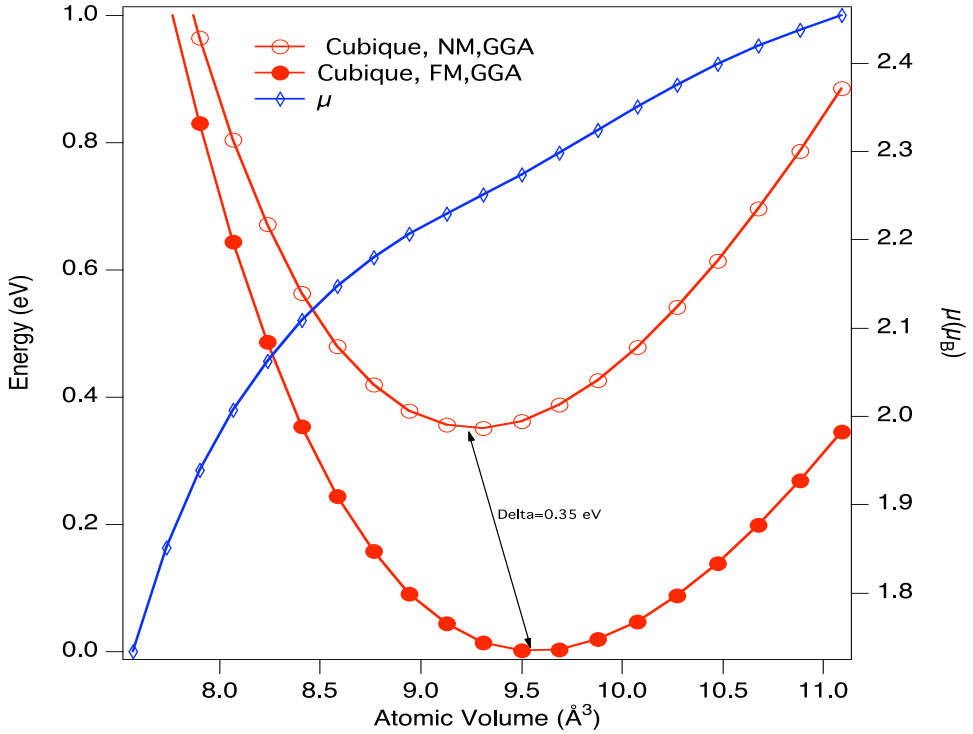
$Co_{1-x}Pt_x$ alloys…

- Overall tendencies…

	a	*μ*
Co	*3.5 (3.5)*	*1.6*
Co_3Pt	*3.7 (3.7)*	*1.4*
$CoPt - L1_0$	*c = 3.7 (3.7)* *a = 3.8 (3.8)*	*1.2 (1.2)*
$CoPt - L1_1$	*a = 3.7* *b = 3.6*	*1.1*
$CoPt - A_2B_2$	*3.8*	*1.1*
$CoPt_3$	*3.9 (3.8)*	*0.7 (0.7)*
Pt	*3.9 (3.9)*	*0*

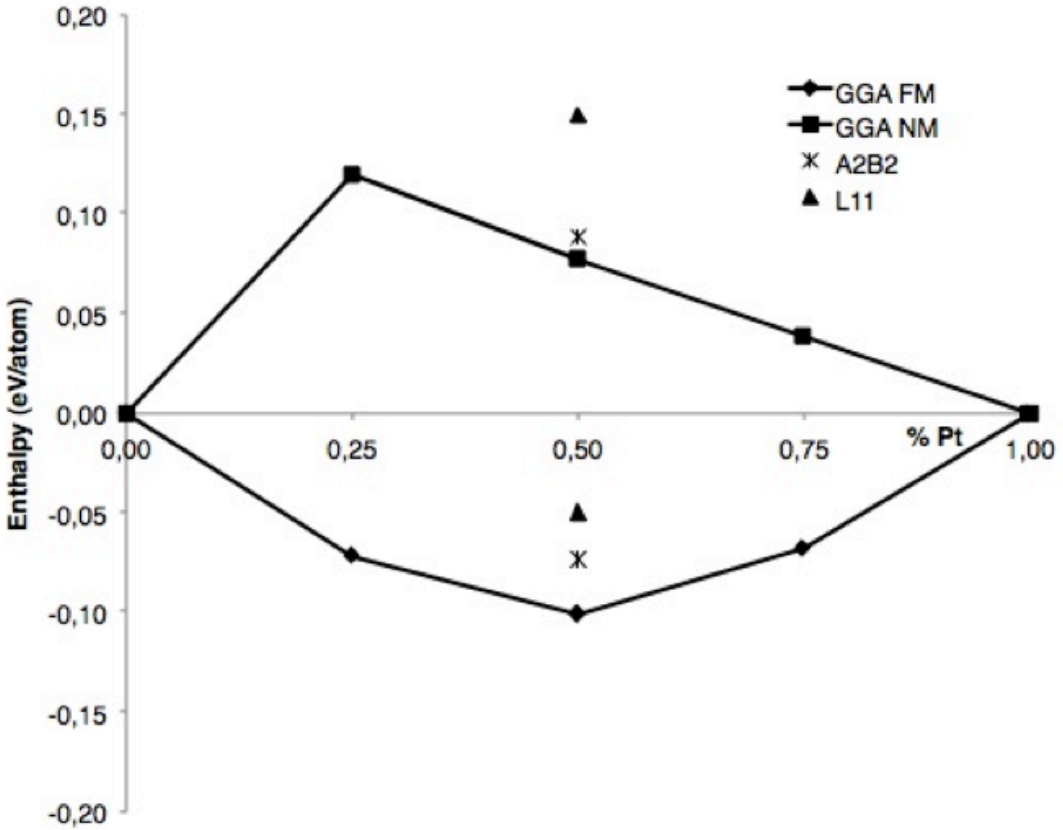
$L1_0$ properties…

- For a ratio c/a=1, the system exhibits a continuous magnetic transition.
- A stabilization of 0.35 eV due to magnetism.



Heats of Formation of $Co_{1-x}Pt_x$

$$\Delta H = \frac{E_{tot}^{Alloy}(nCo,mPt) - nE_{tot}^{Co} - mE_{tot}^{Pt}}{n+m}$$



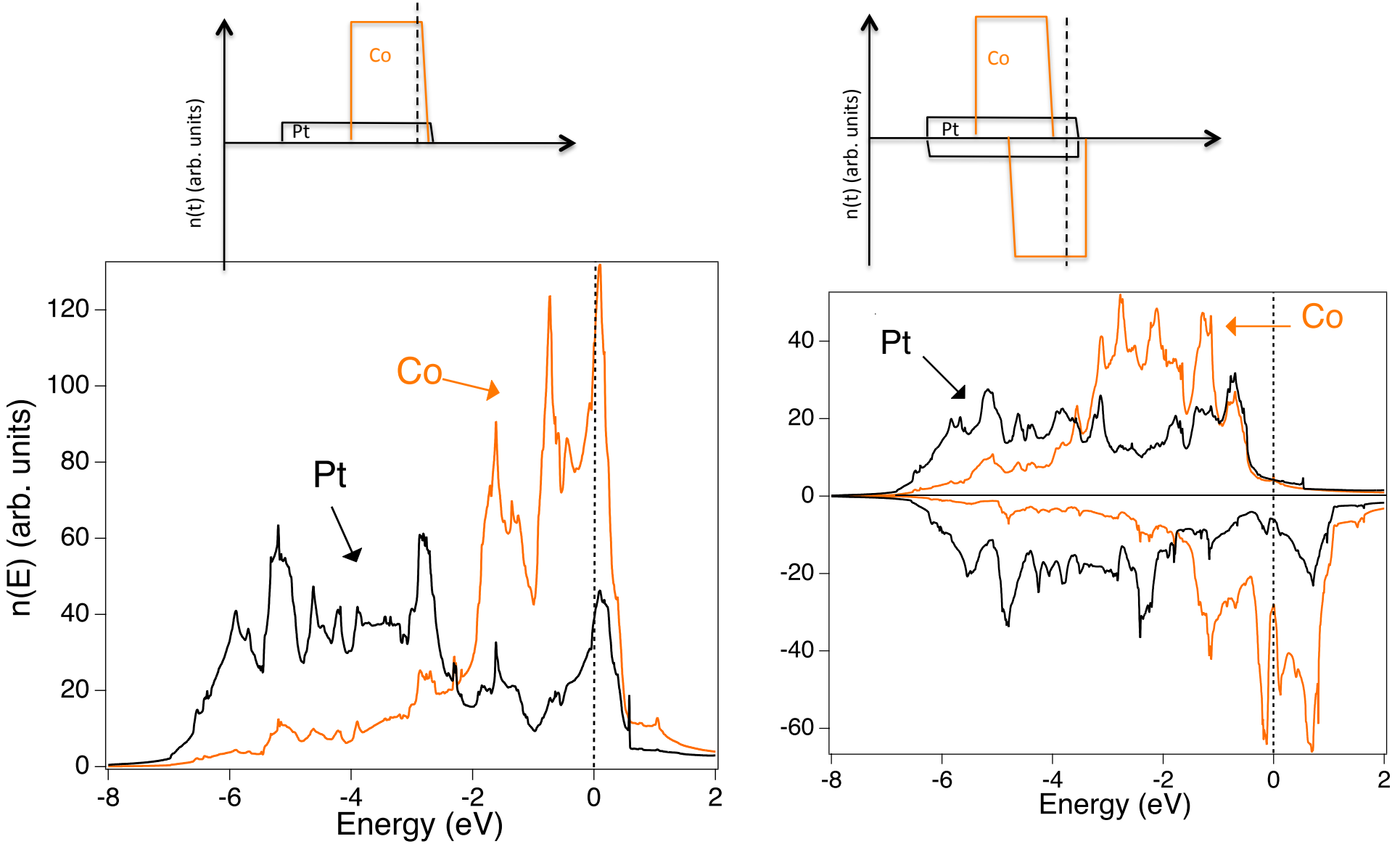
-GGA FM and NM calculations.
-L10,L12, A2B2, L11.

$$\Delta H_{NM} \geq 0$$

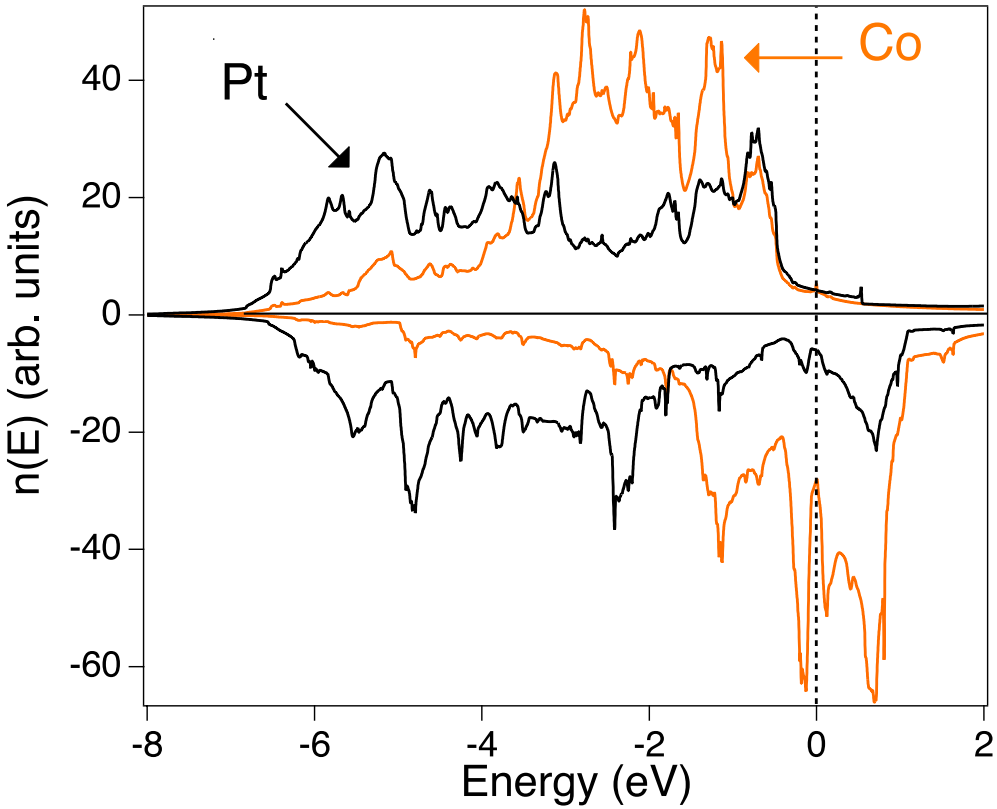
$$\Delta H_{FM} \leq 0$$

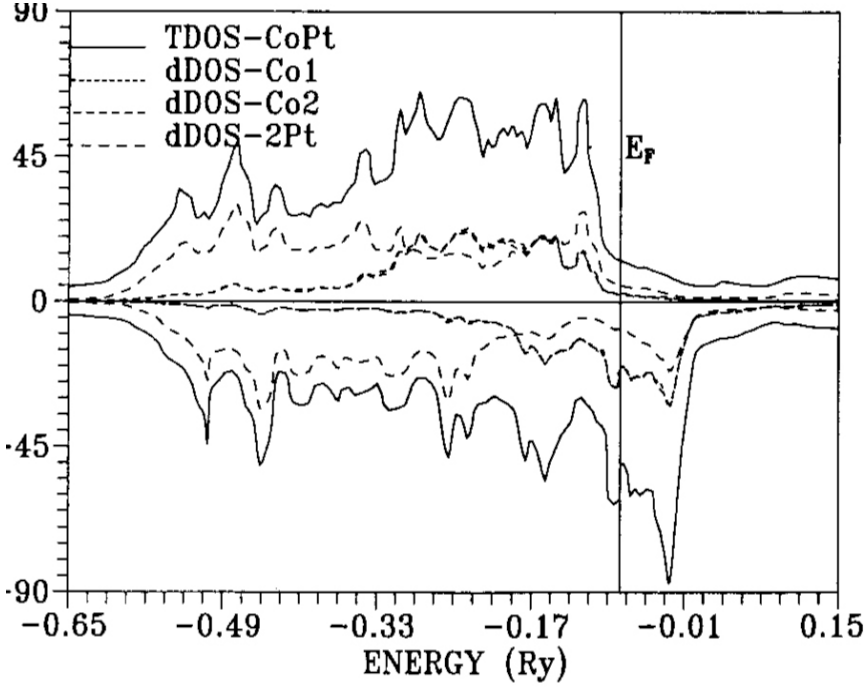
-At 50:50 Co to Pt, L10 is more stable than A2B2 than L11.

DOS….


Co
Pt
n(t) (arb. units)
Co
Pt
n(t) (arb. units)
n(E) (arb. units)
Co
Pt
Energy (eV)
Pt
Co
Energy (eV)

DOS….

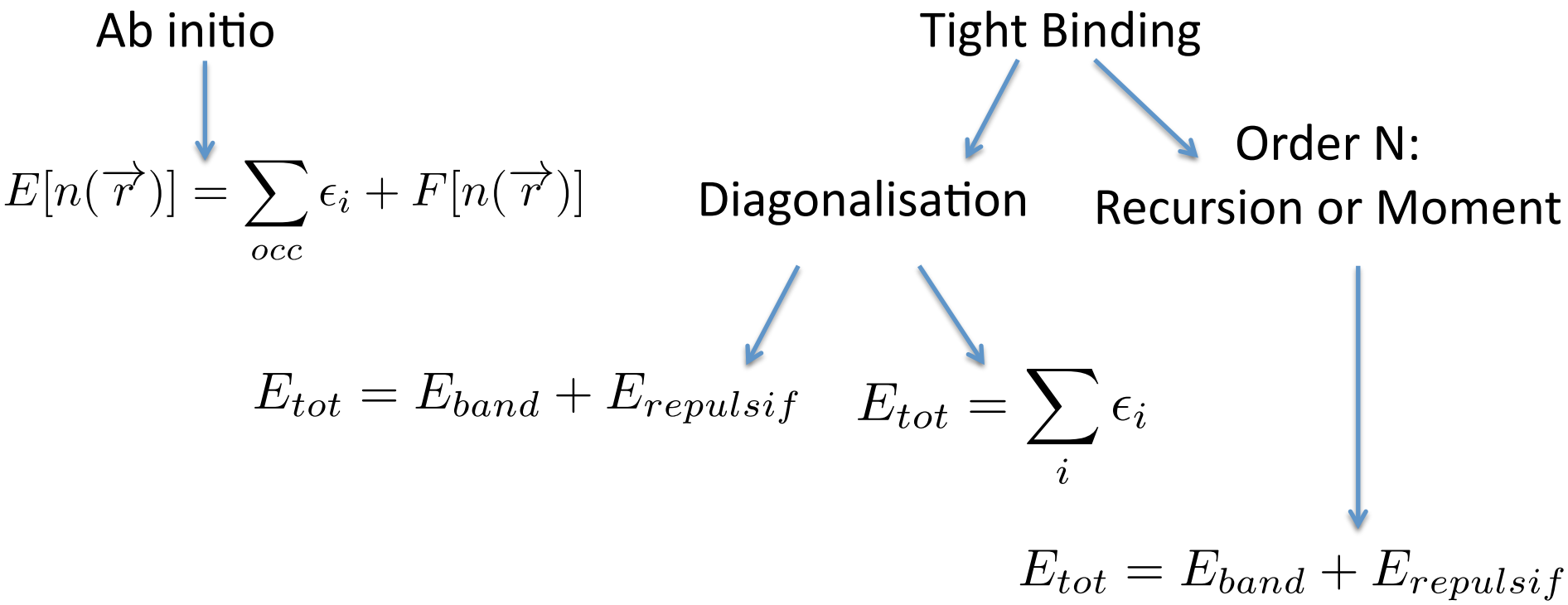




Kashyap *et. al*

1. Co and Pt in the elemental bulk form ab initio
2. $Co_{1-x}Pt_x$ in the alloyed bulk form:
   - GGA calculations in the PAW approximation.
3. Construction of a simple interatomic potential

Total Energy Methods

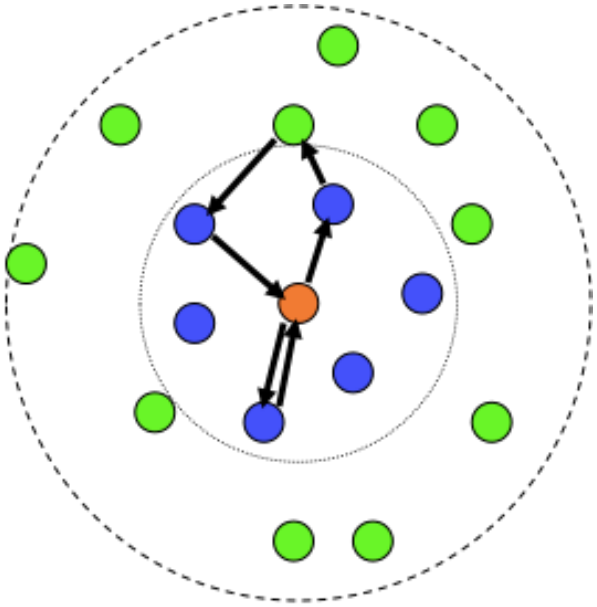


Which method ?

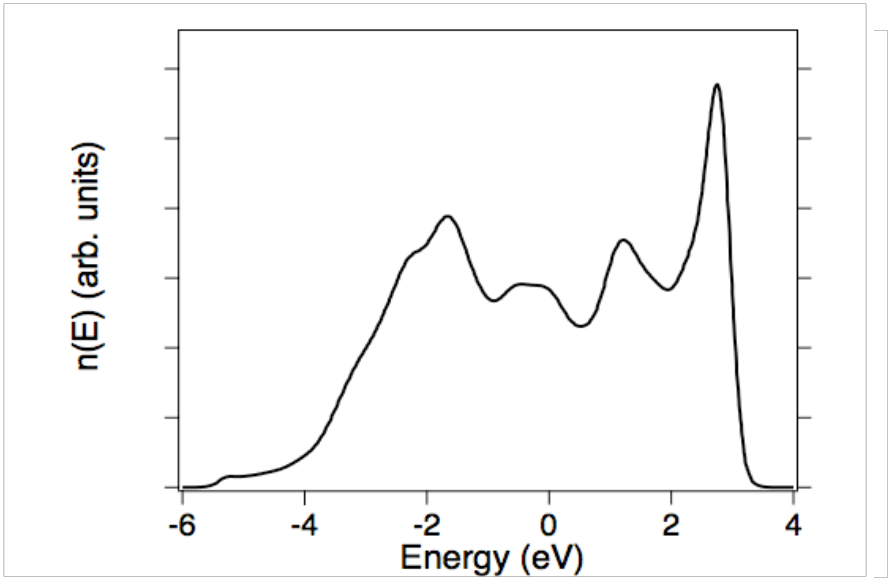
- Long term goals:
  - Structure relaxation
  - Multi scale studies

Semi-Empirical Moments theorem

- A local description of the environment => LDOS



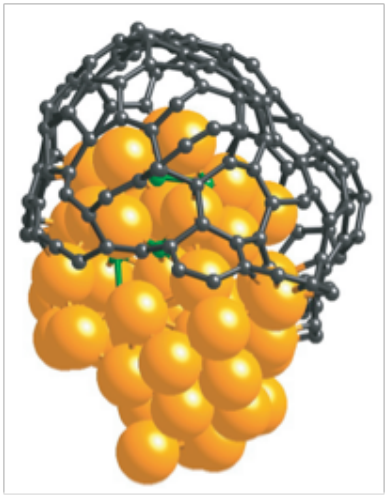
- 30th moment



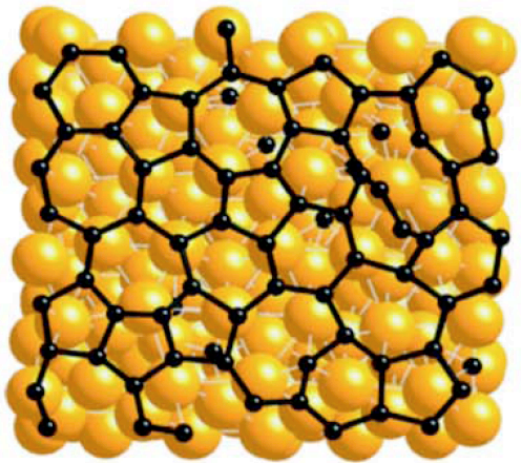
- The LDOS on the red atom depends on the:
  - 1st neighbors blue neighbors (2nd moment approximation).
  - 1st and 2nd green neighbors (4th moment and up)

Fourth moment approximation

- Works for Carbides (NiC)
  - Minimal basis set : C (s and p electrons), Ni (d electrons)
    - Moment method
    - Empirical repulsive term
  - Tight-Binding model implemented in a Monte Carlo code
    - Canonical and Grand Canonical ensembles



Nucleation of carbon nanotube from a Ni nanoparticle



Formation of graphene from a Ni slab

H. Amara, J.-M. Roussel, C. Bichara, J.-P. Gaspard and F. Ducastelle, PRB 79, 014109 (2009)

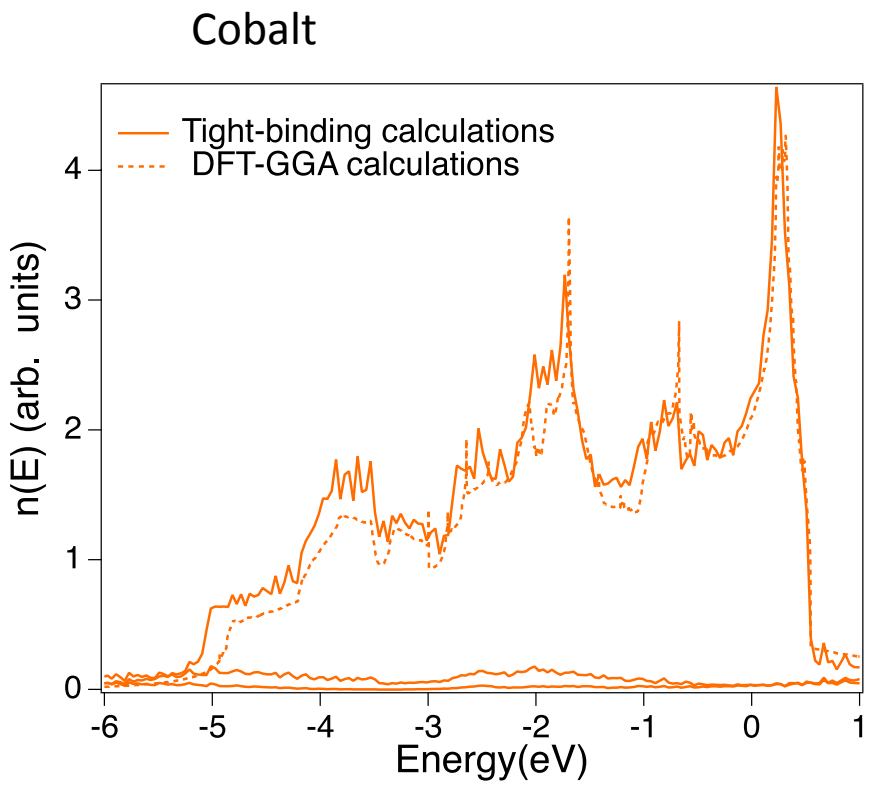
S. Karoui, H. Amara, C. Bichara and F. Ducastelle ACS Nano 4, 6114 (2010)

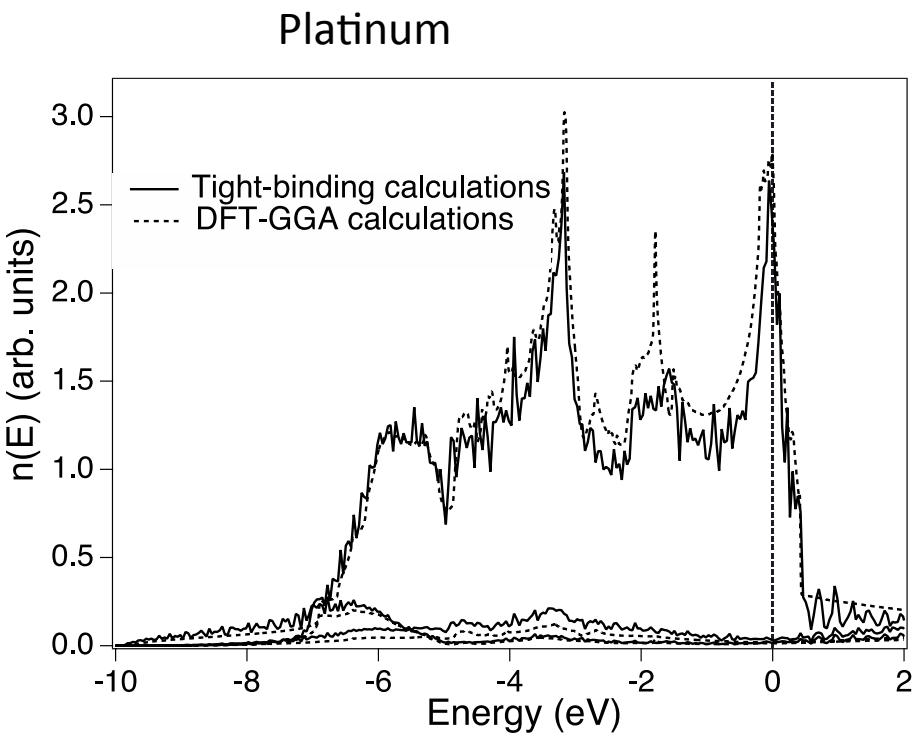
Fourth moment approximation

- Can this approach be transfered to transition metal alloys?
  - Are magnetic transitions correctly reproduced in band d models?
  - Is the fourth moment sufficient in order N methods?

Full diagonalisation

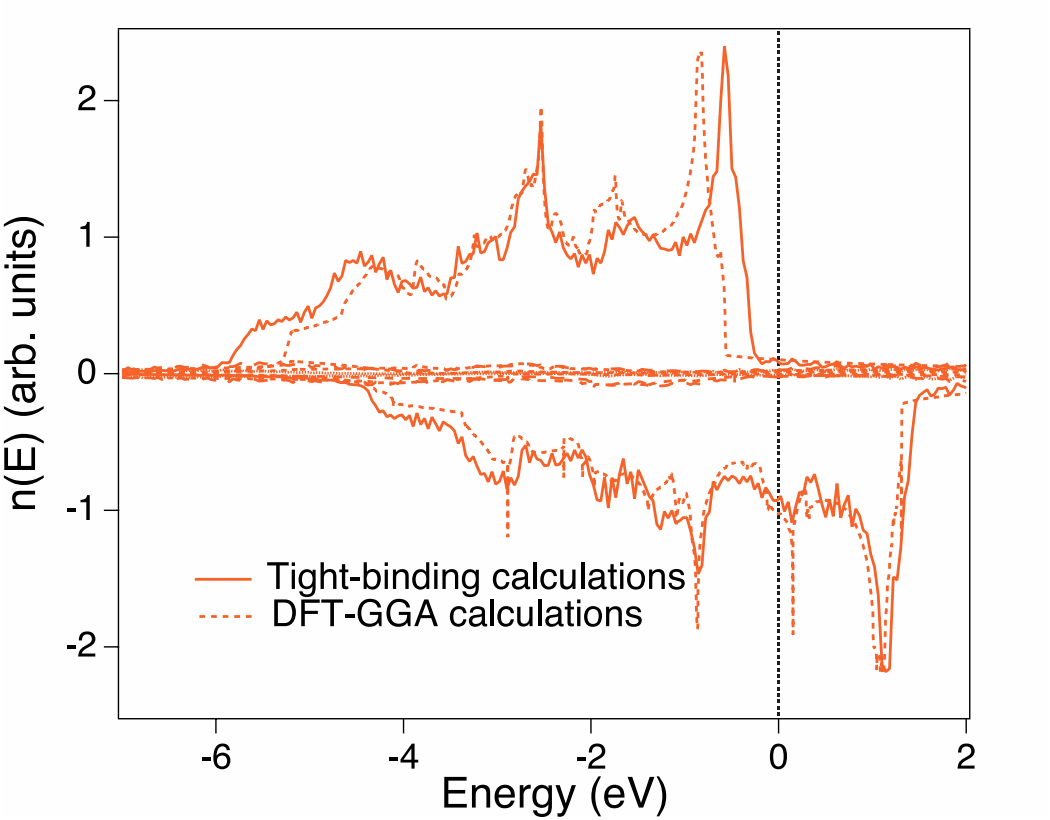
- S-p-d: Band structure, DOS….





Full diagonalisation

- Magnetism in s-p-d :



Stoner-Wolfarth Model

$$H_{ech} = \frac{I}{2} m_s$$

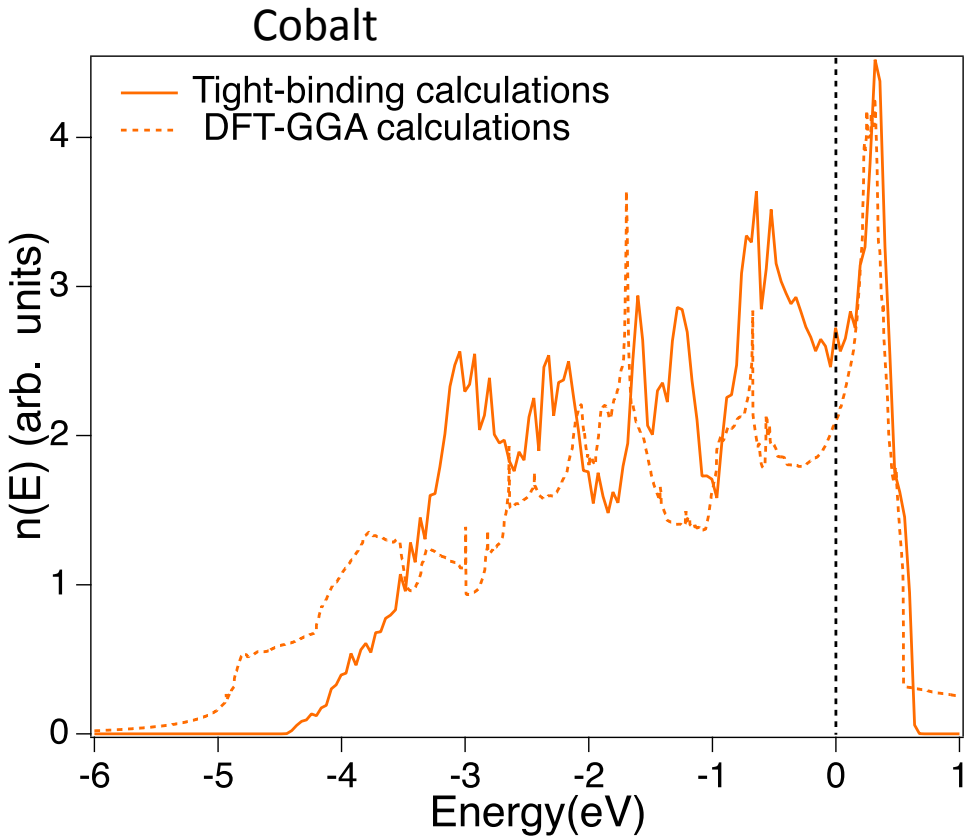
$$\epsilon_\uparrow = \epsilon^0 - \frac{I}{2} m_s$$

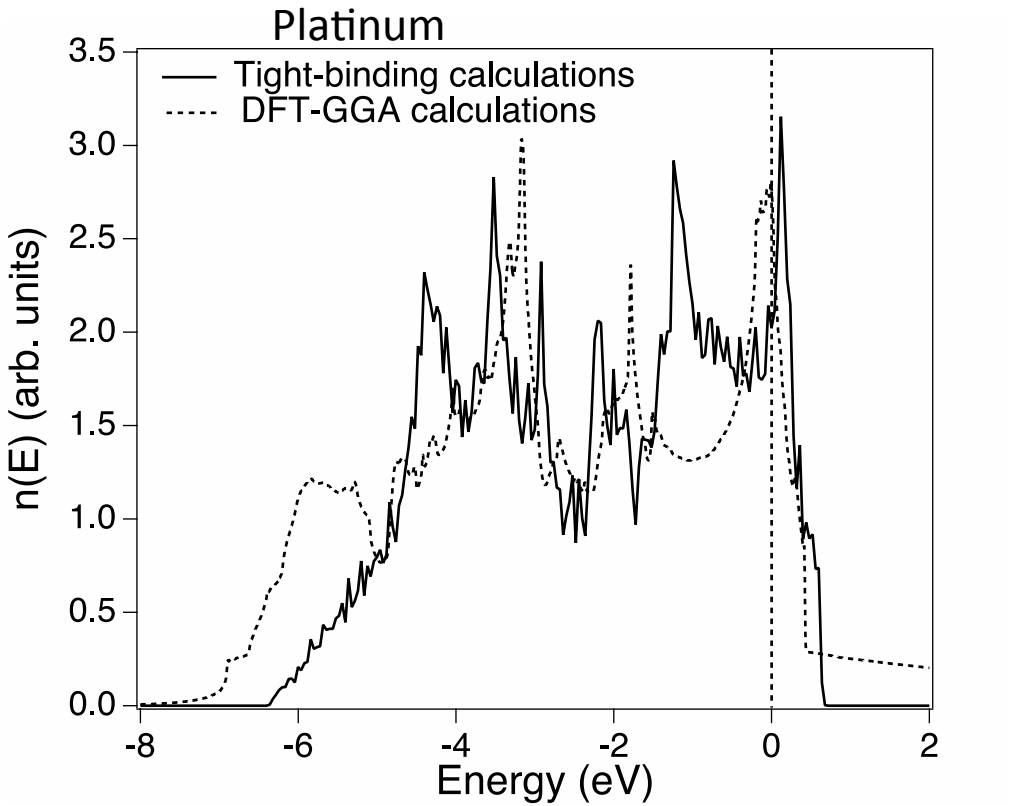
$$\epsilon_\downarrow = \epsilon^0 + \frac{I}{2} m_s$$

	E_{shift}	μ (μ_B)
Tight Binding	1.7 eV	1.66
DFT-GGA	1.9 eV	1.64

Full diagonalisation

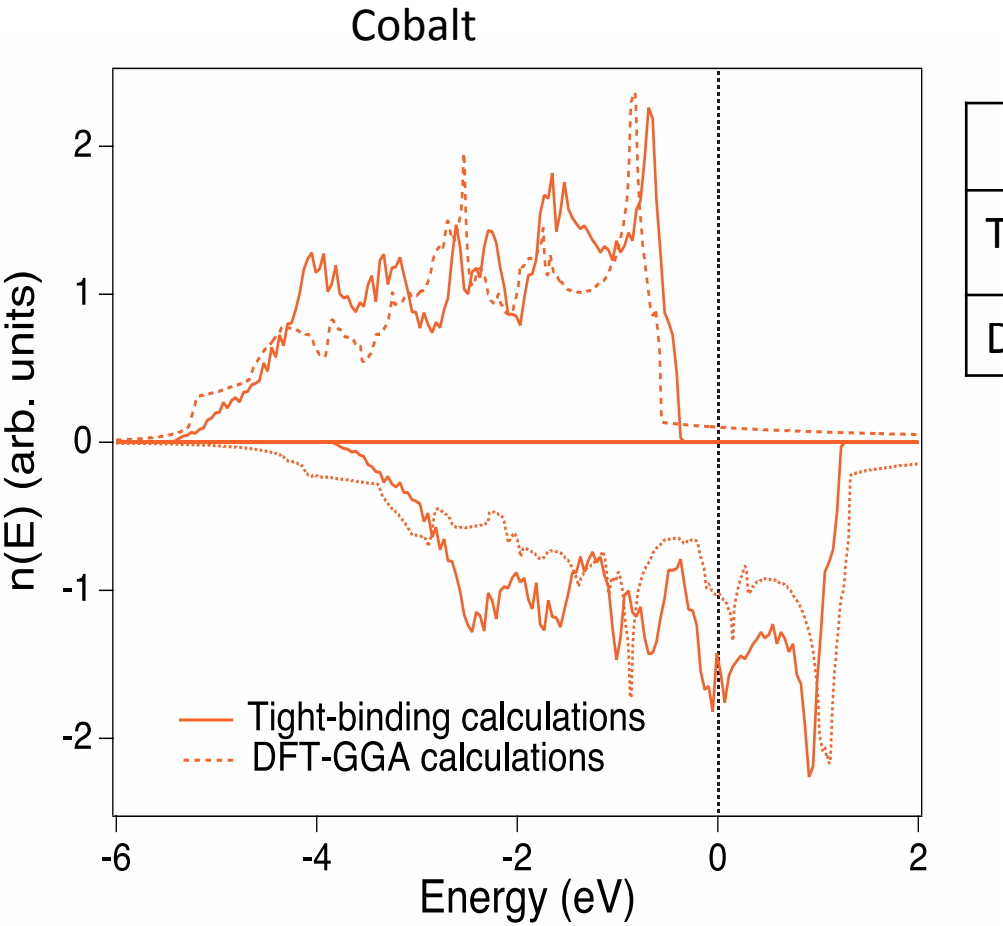
- In d only:
  - SB and DOS correctly reproduced





Full diagonalisation

- Magnetism in d :



	E_{shift}	μ (μ_B)
Tight Binding	1.7 eV	1.69
DFT-GGA	1.9 eV	1.64

Conclusions and Perspectives

- Magnetism does stabilize the $Co_{1-x}Pt_x$.
  - Best results from GGA FM calculations in the PAW formalism.

- Magnetism can be correctly described by a band d tight binding scheme.

- Fourth moment tight binding model:
  - Order-disorder transitions in nanoalloys.
  - Magnetic contributions in the transition.