Quantum-Based Theories of Condensed Matter

Emily A. Carter

MAE, PACM, Chemistry, Chemical Engineering,
PRISM, PICSciE

Princeton University

4 Talks:

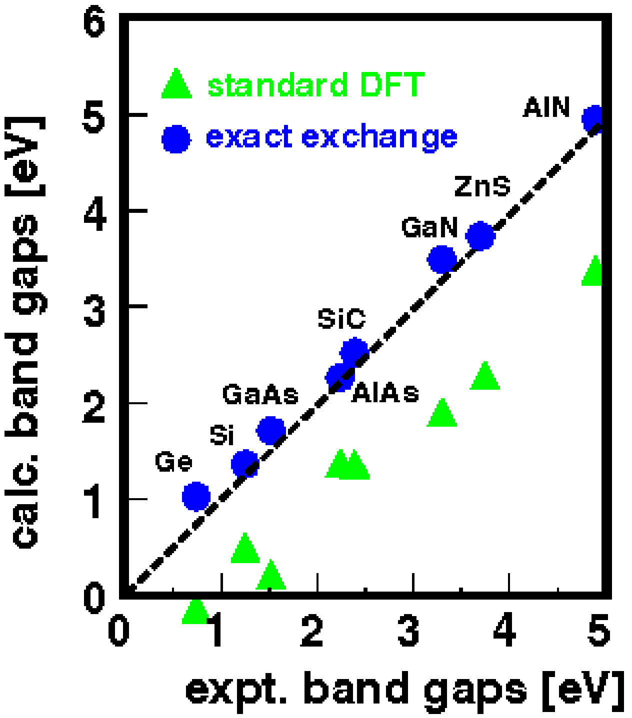
- Introduction to Periodic Density Functional Theory & Spin-Dependent Pseudopotential Theory for Open-Shell and Magnetic Systems
- Materials Applications of Periodic DFT: Corrosion & Protection of Metals
- Linear Scaling Orbital-Free DFT: Present and Future
- Quantum-Based Multiscale Modeling of Materials

For talk #1, thanks to: **Dr. Vincent Cocula (COMSOL, Inc.)**
Dr. Patrick Huang (Princeton)
Dr. De-en Jiang (UCLA/Princeton -> ORNL)
Mr. Greg Ho (Princeton)

Condensed Matter Electronic Structure Theory

- Sometimes periodic Hartree-Fock theory, but mostly periodic Density Functional Theory, since generally more accurate (though it most definitely can fail!)

- Failures of DFT – physics missing or incorrect:
  - Strongly correlated systems (late transition metal oxides, sulfides, actinides, etc.)
  - Van der Waals interactions
  - Excited states
  - Band gaps
  - Open shell systems

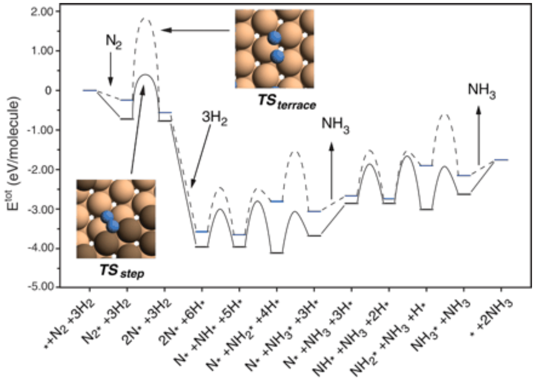


After R. Martin

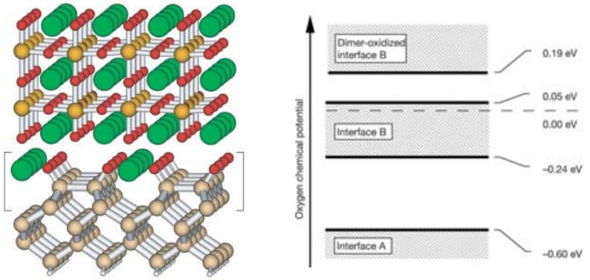
But…often works exceedingly well: depends on property and material of interest!

Example Applications Where it (Often) Works Well!

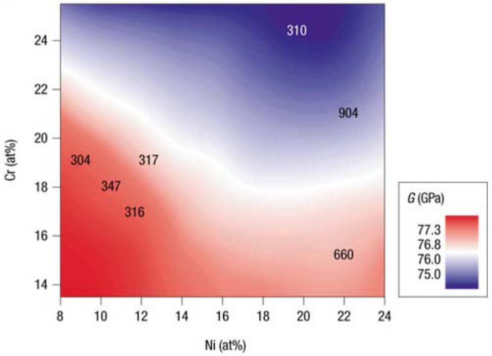
- ☐ Surface chemistry and heterogeneous catalysis
  - Adsorbate structure and energetics
  - Metals, ceramics, semiconductors, zeolites, etc.
  - Reaction pathways and transition states
- ☐ Materials science
  - Bulk, surface, interface, defects
  - Electronic structure
  - Mechanical properties
  - Magnetic properties



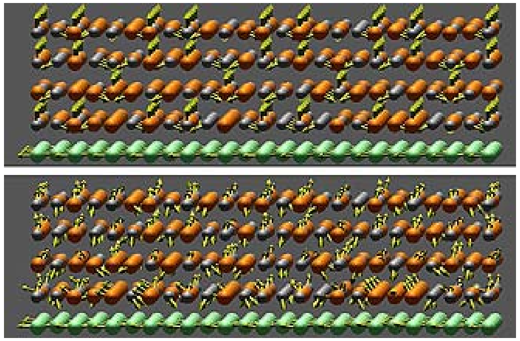
"NH_3 synthesis", Honkala et al., Science, 2005



"Interface between Si and a high-k oxide", Blöchl et al., Nature, 2004



"Stainless steel optimization from DFT", Vitos et al., Nature: materials, 2002

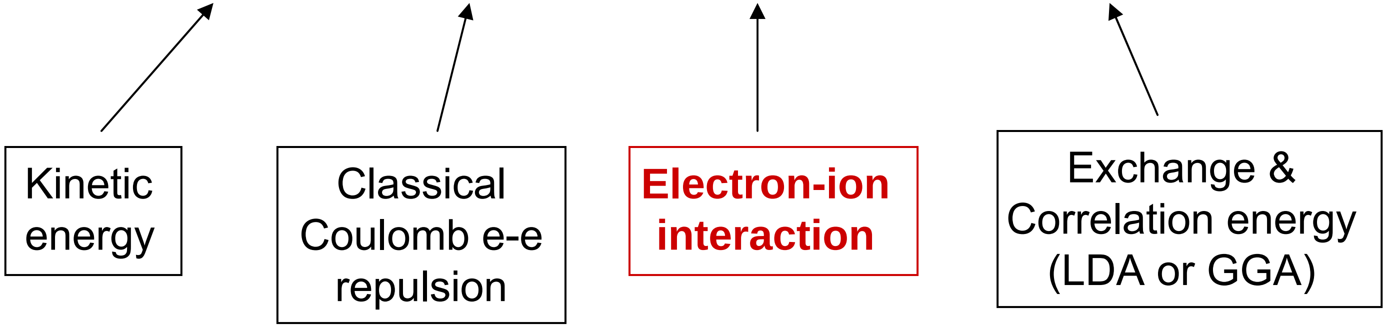


"Spin dynamics of FeMn/Co(111)"
Oak Ridge National Laboratory

Solid State Density-Functional Theory (DFT)

Ground state total energy expressed as a functional of the density *n*.

$$E[n] = T_{\mathrm{s}}[n] + E_{\mathrm{H}}[n] + E_{\text{e-ion}}[n] + E_{\mathrm{xc}}[n]$$



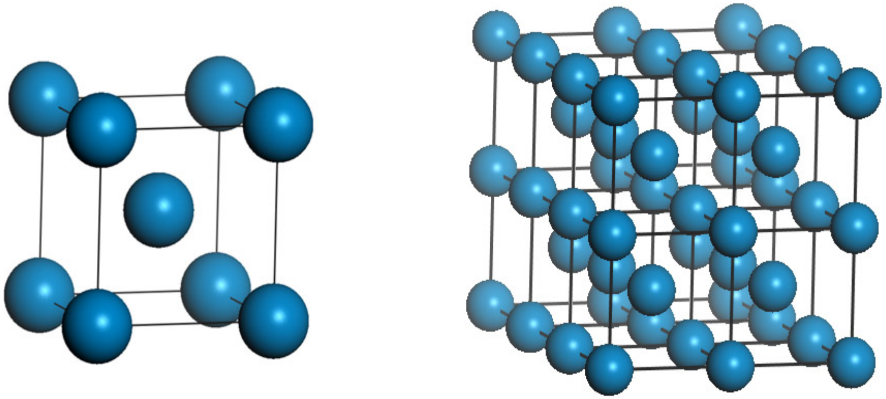
Kinetic energy

Classical Coulomb e-e repulsion

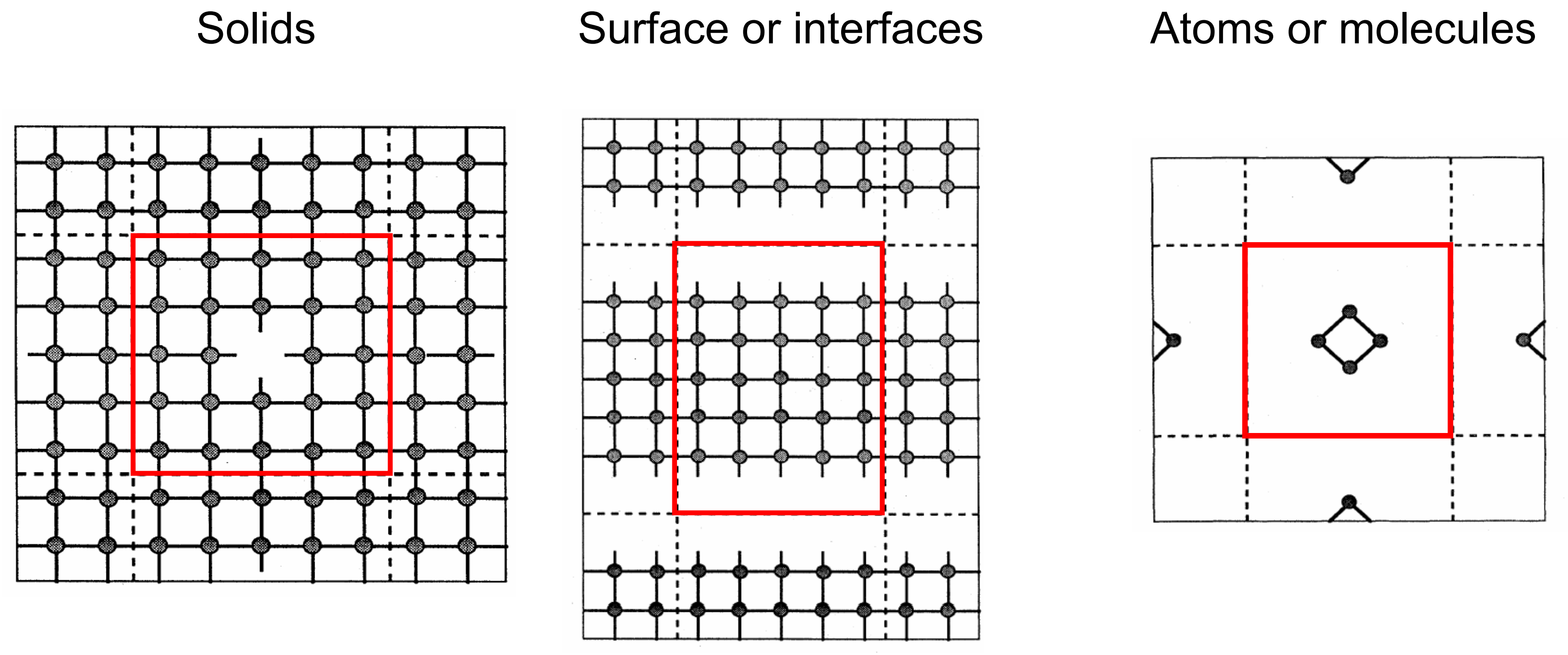
Electron-ion interaction

Exchange & Correlation energy (LDA or GGA)

- 3D periodic boundary conditions
- Planewave (PW) basis set
- K-point sampling of Brillouin zone
- Pseudopotentials
- Spin-polarized “Wavefunctions”



Supercell method



Solids

Surface or interfaces

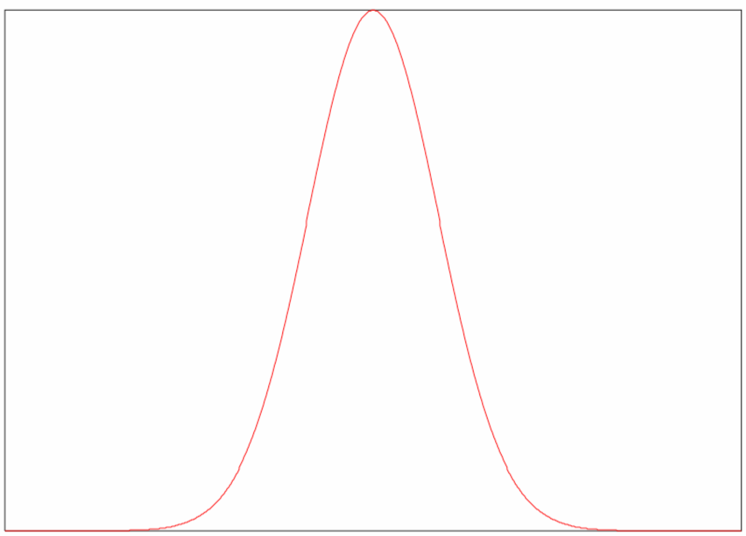
Atoms or molecules

After Payne et al., Rev. Mod. Phys., 1992.

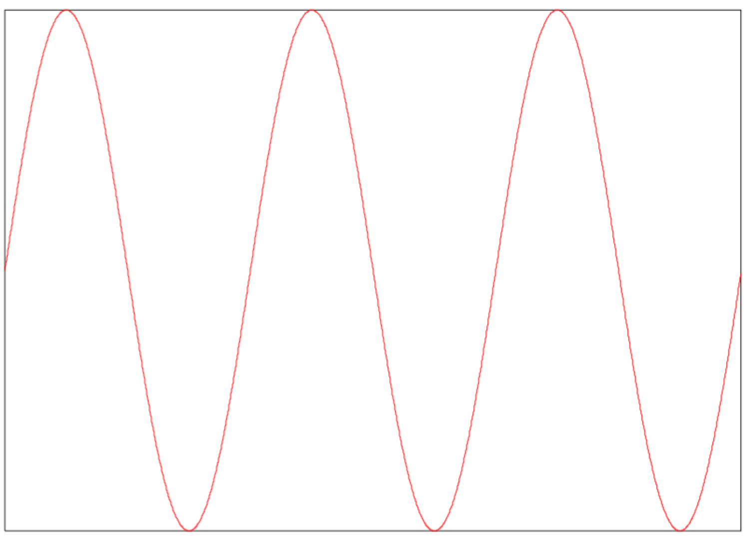
☐ Impose periodic boundary conditions to describe extended, translationally ordered (periodic) bulk crystals, surfaces, and interfaces. Can also use same formalism to describe molecules.

Basis set choice depends on symmetry of system

- For electrons in isolated atoms and molecules, typically use localized basis sets, e.g. atom-centered Gaussian functions (**spherical symmetry**)



- Plane waves provide a natural representation of electrons in bulk solids (**translational symmetry**)



Planewave basis sets

Bloch’s theorem: electronic wavefunction in a periodic potential consists of a wave-like part and a cell-periodic part $f_i(\mathbf{r})$: Think of nearly free electron in a periodic potential

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

k is a momentum quantum number associated with translational motion in a periodic crystal, (consider E(k) for a free electron)

The cell-periodic part can be expanded in a discrete plane-wave basis, given by the reciprocal lattice vectors **G** of the crystal:

$$f_n(\mathbf{r}) = \sum_{\mathbf{G}} c_{n,\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \Rightarrow \psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n,\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

Need to truncate the expansion! Keep only planewaves below E_{cut}:

$$\frac{1}{2}\left|\mathbf{k}+\mathbf{G}\right|^2 \le E_{cut}$$

K-point sampling

Need to evaluate integrals in k-space of the form:

$$I \propto \int d\mathbf{k}\, f(\mathbf{k}) \approx \sum_{n} w_n\, f(\mathbf{k}_n)$$

Example: charge density

$$\rho(\mathbf{r}) = \sum_{n} \int d\mathbf{k} \left| \psi_{n\mathbf{k}}(\mathbf{r}) \right|^2$$

An efficient k-space quadrature rule exploits the symmetry of the lattice with the minimal number of points k_n (Monkhorst and Pack, 1976)

In practice, one should systematically vary the number of k-points until properties of interest are converged!

DFT Energy Terms for a Periodic System

Kinetic Energy

$$T_S[\rho] = \sum_n \int \phi_n^*(\vec{r})\left(-\frac{1}{2}\nabla^2\right)\phi_n(\vec{r})d\vec{r} = \frac{\Omega}{2}\sum_{\vec{k},\vec{G}}\left|c_{n,\vec{k}+\vec{G}}\right|^2\left(\vec{k}+\vec{G}\right)^2$$

Ion-Electron (Pseudopotential) Energy

$$E^{\text{ion}} = \Omega\sum_{\mathbf{G}} S(\mathbf{G})v^{\text{ps}}(\mathbf{G})n(\mathbf{G}) \qquad S(\mathbf{G}) = \sum_{\mu} e^{i\mathbf{G}\cdot\mathbf{R}_\mu}$$

Hartree (Electron-Electron Repulsion)

$$E^{Hart} = J(\rho) = \frac{\Omega}{2}\sum_{\vec{G}\neq 0}\frac{4\pi}{G^2}\rho(\vec{G})\rho(-\vec{G})$$

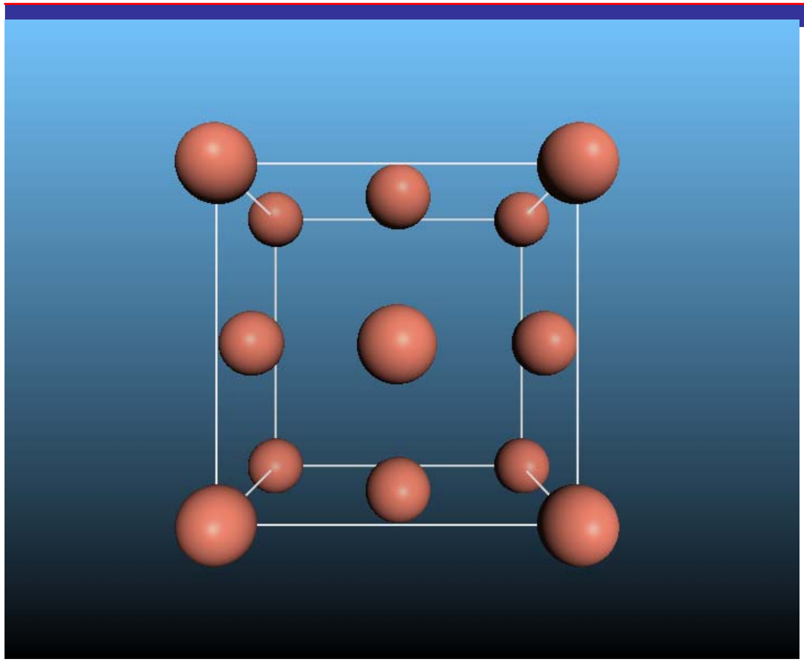
Electron Exchange-Correlation

$$E_{xc}[\rho] = \int \rho(\vec{r})[\varepsilon_x(\rho(\vec{r})) + \varepsilon_c(\rho(\vec{r}))]d\vec{r}$$

Ewald (Ion-Ion)

$$E_{II}^{Ewald}(\{R_I\}) = \frac{1}{2}\sum_{\vec{L}}\sum_{I,J}{}' Z_I Z_J \left.\frac{erfc(\eta|\vec{x}|)}{|\vec{x}|}\right|_{\vec{x}=\vec{L}+\vec{R}_I-\vec{R}_J} + \sum_{G\neq 0}\frac{2\pi}{\Omega}\frac{e^{-G^2/4\eta^2}}{G^2}\left|\sum_I Z_I e^{iG\cdot R_I}\right|^2 - \frac{\pi}{2\eta^2\Omega}\left(\sum_I Z_I\right)^2 - \frac{\eta}{\sqrt{\pi}}\sum_I Z_I^2$$

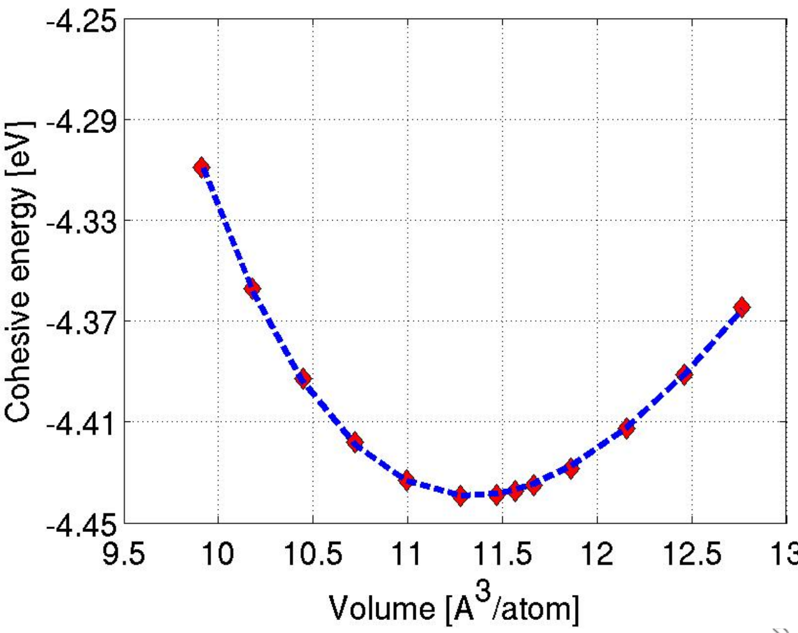
Bulk crystals: FCC Cu



Single-point energy calculation:

1. Exchange-correlation: LDA or GGA
2. Choose pseudopotential
3. Set the unit cell lattice constant
4. Position ions within unit cell
5. Choose a plane-wave cutoff E_{cut}
6. Choose k-points
7. Choose Fermi surface smearing width

FCC Cu equation of state



Parameters to converge:

1. k-point mesh
2. plane-wave cutoff E_{cut}
3. Fermi surface smearing width

Equilibrium unit cell volumes for bulk solids

Solid	Expt. [a_0^3]	LDA [a_0^3]	GGA [a_0^3
NaCl	302.7	276.1	313.1
Si	270.0	266.2	276.3
Ge	305.9	301.4	322.1
GaAs	304.3	298.3	320.5
Na	255.4	224.4	249.8
Al	112.1	106.6	111.2
Fe	79.5	70.5	76.7
Cu	78.7	73.5	80.6
Pd	99.3	95.5	103.2
W	106.5	104.0	108.9
Pt	101.3	99.7	105.7
Au	112.8	111.9	121.1

LDA typically underestimates equilibrium volumes:
LDA overbinds everything…
Can trace back to poor description of an atom…
GGA tends to overcompensate and underbind…

S. Kurth, J. P. Perdew, and P. Blaha, International Journal of Quantum Chemistry, 75, 889 (1999).

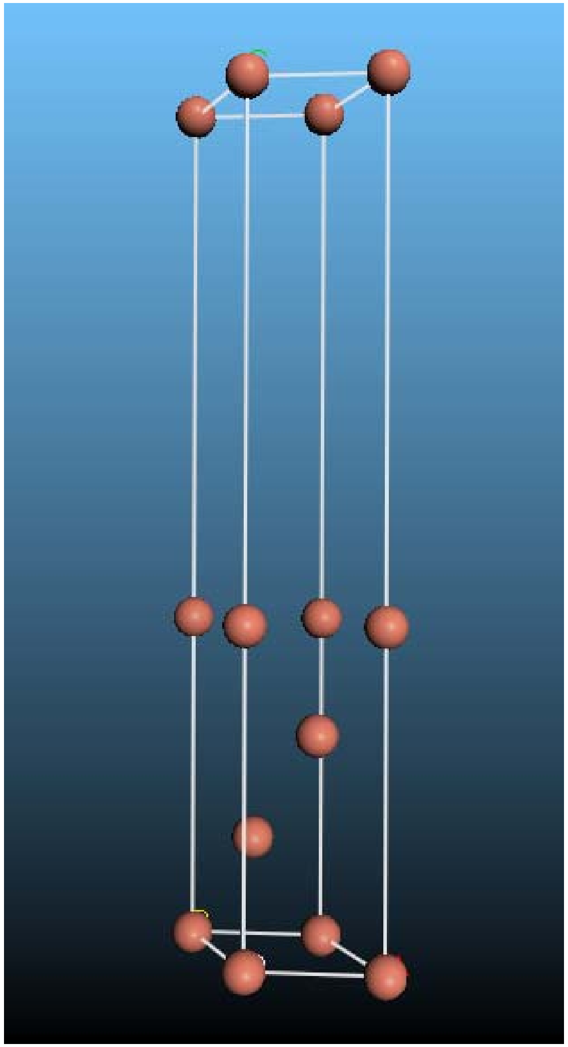
Equilibrium bulk moduli for solids

Solid	Expt. [GPa]	LDA [GPa]	GGA [GPa]
NaCl	24.5	32.2	23.4
Si	98.8	97.0	89.0
Ge	76.8	71.2	59.9
GaAs	74.8	74.3	60.7
Na	6.9	9.2	7.6
Al	77.3	84.0	77.3
Fe	172	259	198
Cu	138	191	139
Pd	181	226	174
W	310	335	298
Pt	283	312	247
Au	172	195	142

LDA typically <u>over</u>estimates bulk moduli, again due to overbinding…

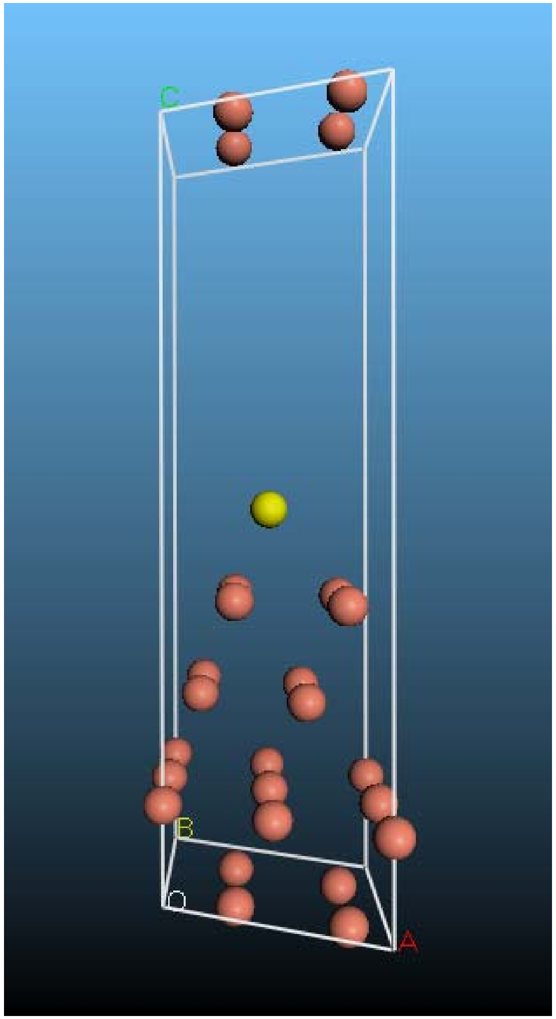
S. Kurth, J. P. Perdew, and P. Blaha, International Journal of Quantum Chemistry, 75, 889 (1999).

Clean surfaces: Cu(111)



- An infinite plane-wave basis is necessary to describe non-periodic system ==> supercell approximation
- For surfaces, introduce a vacuum layer between slabs
- Need to check convergence with respect to vacuum thickness, and number of substrate layers

Adsorbates: e.g. Co/Cu(111)



- Increase unit cell in lateral directions to simulate isolated adsorbates or fractional coverage (surface concentration < 1)

- Co is magnetic ==> need to use a spin-dependent E_{xc}

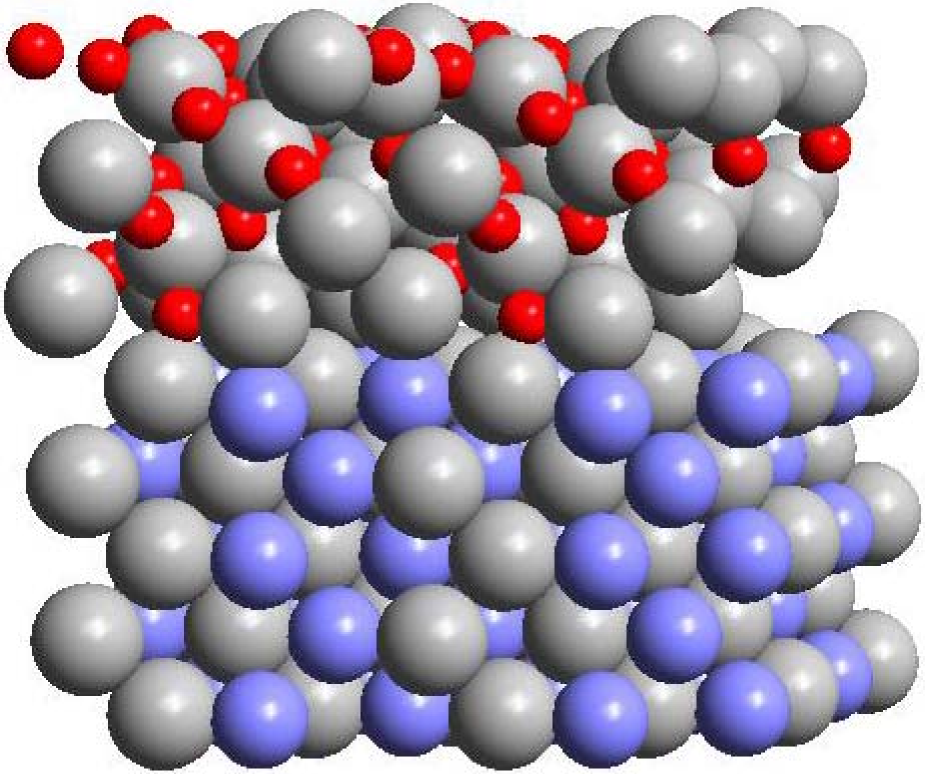
- Must correct energy for any dipole formed...

- Localized Co electrons hybridize with Cu band states to form extended singlet--"Kondo cloud", which we are modeling currently within a CI/DFT embedding theory (Huang)

Interfaces: Al_2O_3/NiAl

- At a surface or interface, ion positions can be quite different from bulk
- Typically modeling a macroscopic substrate with a thin film on top. Use equilibrium lattice vectors for substrate, force film to adjust…
- Must worry about lattice matching of heterogeneous materials – do not want to choose periodic cells that induce too much artificial strain
- Minimum-energy structure found using energies and gradients from DFT; need dipole corrections..

Al_2O_3 film



NiAl substrate

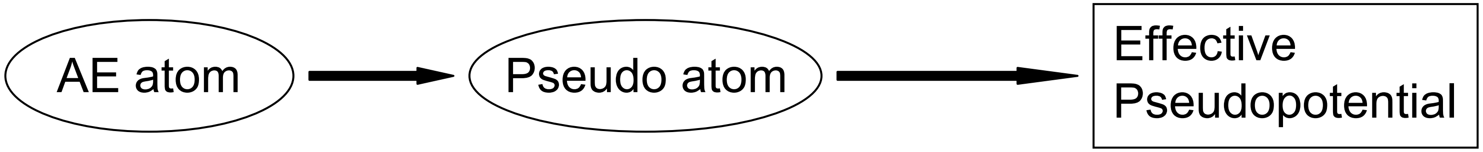
Electron-Ion interaction: Pseudopotential Theories

All-electron theories (AE)

- All electrons in system explicitly treated
- Full featured wavefunction
- Mixed basis set to augment PWs around nuclei

Pseudopotential theories (PsP)

- Remove inert core electrons
- Only valence electrons considered in DFT equations
- Smooth screened potential to mimic core+nucleus



Pseudopotential generation

Generated from first-principles

Input
- atomic species
- valence states
- level of DFT theory (LDA or GGA)

- Solve atomic all-electron DFT equations

$$\left(\hat{T} + V^{\mathrm{AE}} - \varepsilon_{nl}\right) |\psi_{nl}\rangle = 0$$

- Pseudization

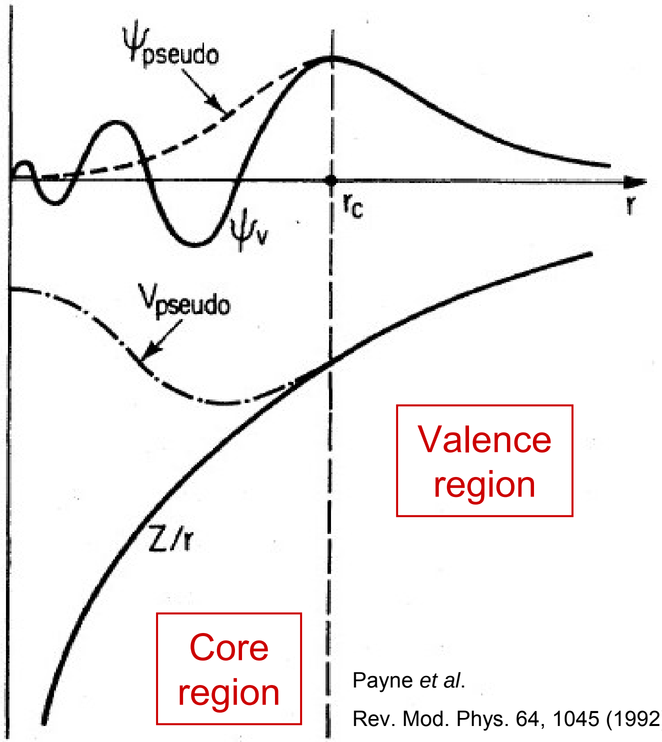
  For each valence state,

  - Pick cutoff radii r_{cl} beyond which will match AE wavefunction
  - Smooth out wavefunctions so contain no radial nodes

$$\psi_{nl} \longrightarrow \phi_{nl}$$

- Invert pseudo atom DFT equations to solve for V^{PS}

$$\left(\hat{T} + V^{\mathrm{ps}} - \varepsilon_{nl}\right) |\phi_{nl}\rangle = 0$$



Payne *et al.*

Rev. Mod. Phys. 64, 1045 (1992)

Classes of Pseudopotentials

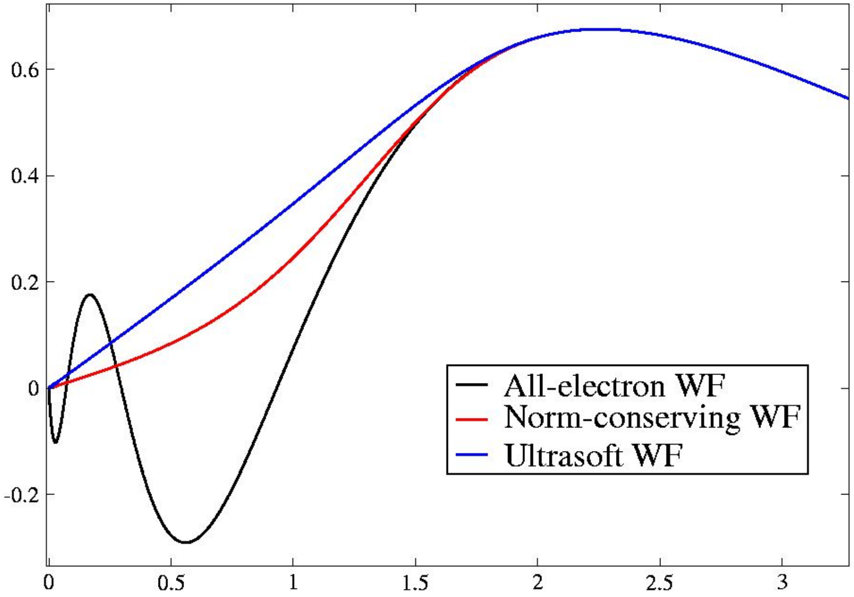
Constraints on pseudowavefunction generation:

- Norm-conserving pseudopotential

$$\langle \phi_{nl} | \phi_{nl} \rangle_{r<r_{cl}} = \langle \psi_{nl} | \psi_{nl} \rangle_{r<r_{cl}}$$

- Ultrasoft pseudopotential

$$\langle \phi_{nl} | \phi_{nl} \rangle_{r<r_{cl}} \neq \langle \psi_{nl} | \psi_{nl} \rangle_{r<r_{cl}}$$



When using ultrasoft pseudopotentials...

- Smoother WFs → smaller basis set → cheaper calculation
- Deficit in electron density recovered by localized augmentation function

$$Q_{nl}(r) = \psi^*_{nl}(r)\psi_{nl}(r) - \phi^*_{nl}(r)\phi_{nl}(r)$$

- Much more complicated general formalism

Recast in KB Form for Use in PW-Based DFT

Inversion of the KS equations to solve for the pseudo-potential

$$\left(\hat{T} + V^{ps} - \varepsilon_i\right)\,|\phi_i\rangle = 0$$

And the ionic pseudo-potential usually written as a sum of local and nonlocal terms

$$v^{ps} = v_{loc} + \sum_l \Delta v_l$$

Long range V_{loc} calc'd in G-space.

Fully nonlocal form used is the one of Kleinman and Bylander:

$$v_{ps} = v_{loc} + \sum_{lm} \frac{|\Delta v_l\,\phi_l\rangle\,\langle\phi_l\,\Delta v_l|}{\langle\phi_l|\,\Delta v_l\,|\phi_l\rangle},$$

where the Δv_l's are

$$\Delta v_l = v_l - v_{loc}$$

Exact for the reference atomic pseudo-wavefunction. Approximate for all other cases. Used because of its ease of evaluation in Fourier space.

First, two 1D integrals:

$$P_l(q) = \int_0^\infty 4\pi r^2\,\Delta v_l \phi_l(r)\,j_l(qr)\,dr$$

$$\begin{aligned}\xi_l &= \langle\phi_l|\,\Delta v_l\,|\phi_l\rangle \\ &= \int 4\pi r^2\,\phi_l^*\,\Delta v_l\,\phi_l\,dr.\end{aligned}$$

Then, the nonlocal energy is:

$$\epsilon^j_{\mathbf{k},n} = \sum \xi_l^{-1}\,Z^*_{lm} Z_{lm}$$

$$Z_{lm} = \sum_G \lambda_{lm}(\mathbf{G}+\mathbf{k})\,c_{(\mathbf{G}+\mathbf{k}),n}$$

$$\lambda_{lm}(\mathbf{G}+\mathbf{k}) = \frac{4\pi i^l}{\sqrt{\Omega}}\,P_l(|\mathbf{G}+\mathbf{k}|)\,Y_{lm}\,e^{i(\mathbf{G}+\mathbf{k})\cdot\tau_i}$$

Pseudopotential Properties

Pseudopotential is approximation to all-electron case, but…

Very accurate
- Comparable accuracy to AE in most cases
- Simpler formalism

Low computational cost
- Perform calculations on ‘real-life’ materials

Allows full advantage of planewave basis sets
- Systematic convergence
- Easy to perform dynamics

Pseudopotential quality measured by its *transferability*

Ability of the PsP to match AE values when put in different chemical environments

PsP for Transition Elements

Use of PsP theory for transition elements challenging
-
Inaccuracies due to PsP larger than other DFT approximations

- LDA expected to over bind by ~1% → lattice parameters off from -2 to +8%
- Magnetism poorly described → wrong relative magnetic phase stability

Problems due to unique nature of transition elements:

- Open-shell systems. PsP's are spin neutral
- Nearly degenerate ns and (n-1)d states
- Presence of semi-core p states.

Distinction between valence and core states difficult

Difficult to capture core relaxation effects

PsP smoothness & accuracy

Sharp and localized d wavefunction

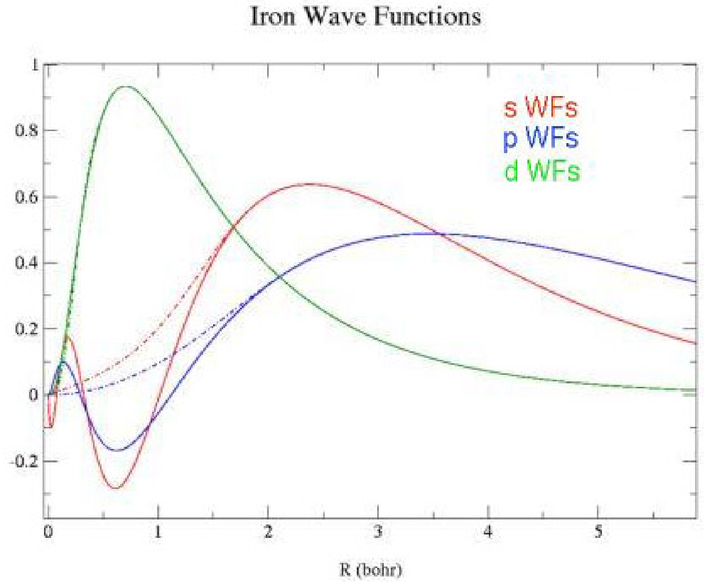
Norm-conserving PsP

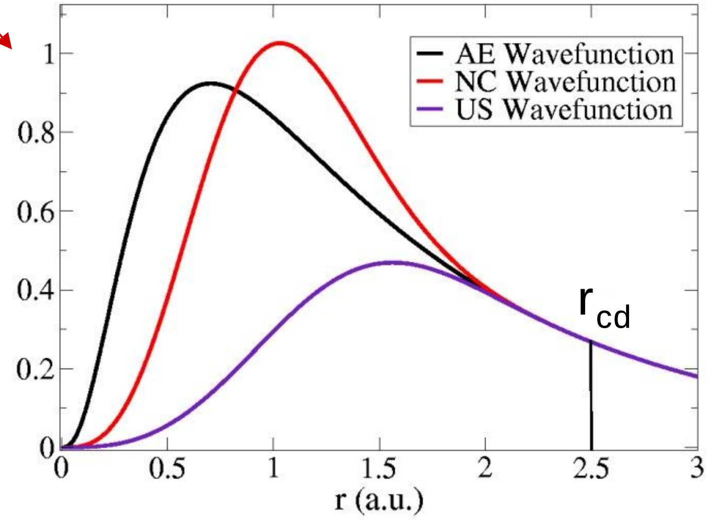
- Move outward cutoff radius to get smoother pseudo-wfn
- Acceptable basis size
- Penalty: decreased transferability

Ultrasoft PsP

- Generate smooth pseudo-wfns
- Possible numerical difficulties to represent augmentation functions

Small cutoff = sharp function
-
Expensive to expand in PWs





Nonlinear Core Correction

Unscreening of total effective potential

$$v_{\text{ion}}^{\text{ps}}(r) = V_{\text{eff}}^{\text{ps}}(r) - v_{\text{H}}[n_v^{\text{at}}] - v_{\text{xc}}[n_v^{\text{at}}]$$

v_{xc} nonlinear function of density: $v_{\text{xc}}[n_c^{\text{at}} + n_v^{\text{at}}] \neq v_{\text{xc}}[n_c^{\text{at}}] + v_{\text{xc}}[n_v^{\text{at}}]$

If recalculate for the atom,
implicit total exchange-correlation:

$$v'_{\text{xc}} = \underbrace{\left(v_{\text{xc}}[n_c^{\text{at}} + n_v^{\text{at}}] - v_{\text{xc}}[n_v^{\text{at}}]\right)}_{\boxed{\textit{Contribution from pseudopotential}}} + v_{\text{xc}}[n_v]$$

$$v'_{\text{xc}} \neq v_{\text{xc}}[n_c^{\text{at}}] + v_{\text{xc}}[n_v]$$

$v'_{\text{xc}} \neq v_{\text{xc}}[n_c^{\text{at}} + n_v]$ ... while it should !

- ➢ Introduction of inherent error
- ➢ Problematic when core and valence atomic densities overlap

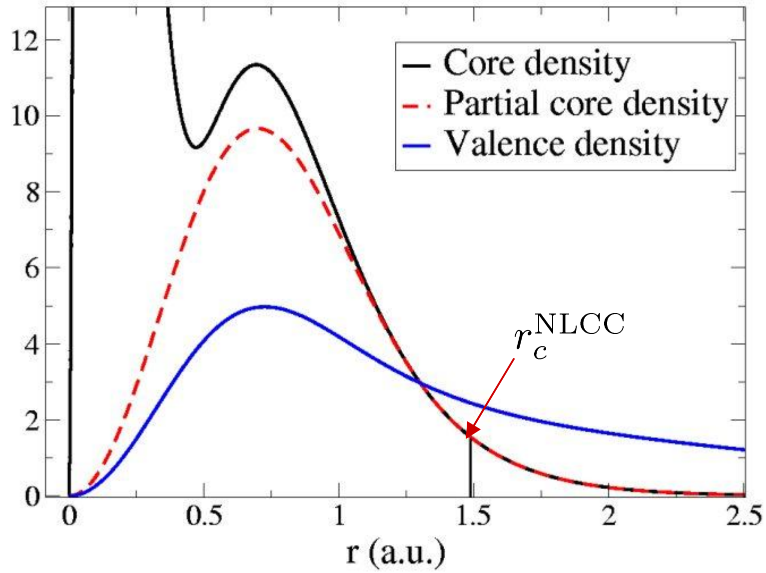
Non-linear Core Correction

Unscreening using smooth function of core density

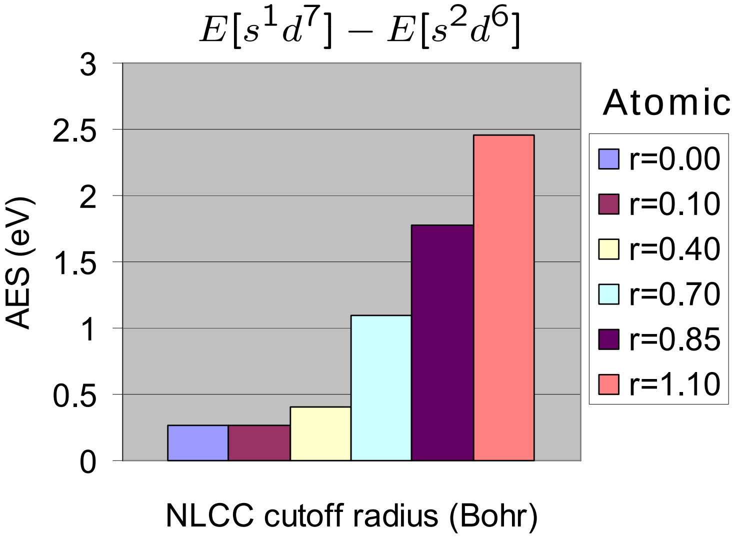
$$v_{\text{ion}}^{\text{ps}} = V_{\text{eff}}^{\text{ps}} - v_{\text{H}}[n_v] - v_{\text{xc}}\left[n_v + n_c^{\text{NLCC}}\right]$$

$$n_{\text{c}}^{\text{NLCC}}(r) = \begin{cases} n_{\text{c}}(r) & \text{for } r > r_{\text{c}}^{\text{NLCC}} \\ \exp\left(\sum_{i=0}^{2} a_i r^{2i}\right) & \text{for } r \leq r_{\text{c}}^{\text{NLCC}} \end{cases}$$

Louie *et al.*, PRB 26, 1738 (1982)



Choice of cutoff radius ?



Cocula *et al.*, JCP 119, 7659 (2003)

Atomic energy splitting (AES) for atomic Fe

- high sensitivity to cutoff choice
- use of full-core improves inaccuracy but impractical
- inaccuracy increases with cutoff

Lack of a unique way to define NLCC
Small cutoffs = too expensive
Large cutoff = inaccurate

To summarize...

Pseudopotential methods for transition metals...

- ... often inaccurate
- ... often highly parameterized (and sensitive to it)
- ... sometimes impractical

Tradeoff between accuracy and cost...

Small cutoffs
=
High accuracy
Expensive potentials

Large cutoffs
=
Low accuracy
Affordable potentials

Need for an accurate and efficient PsP method for transition metals

Spin-Dependent PsP theory

GOAL
- Transferability with a minimum number of adjustable parameters

METHOD
- Multi-reference pseudopotential
- Mimics core polarization

- Conventionally: $E^{\text{ion}} = \int 4\pi r^2\, v(r)\, \left[n^{\uparrow}(r) + n^{\downarrow}(r)\right]\, dr$
- We want: $E^{\text{ion}} = \int 4\pi r^2\, \left[v^{\uparrow}(r)n^{\uparrow}(r) + v^{\downarrow}(r)n^{\downarrow}(r)\right]\, dr$

Potential updated self-consistently with local spin polarization

$$\begin{cases} v^{\uparrow}(r) = v^{o}(r) + F\left[\beta(r)\right]\, \delta v(r) \\ v^{\downarrow}(r) = v^{o}(r) + F\left[-\beta(r)\right]\, \delta v(r) \end{cases}$$

Reference potential

perturbation

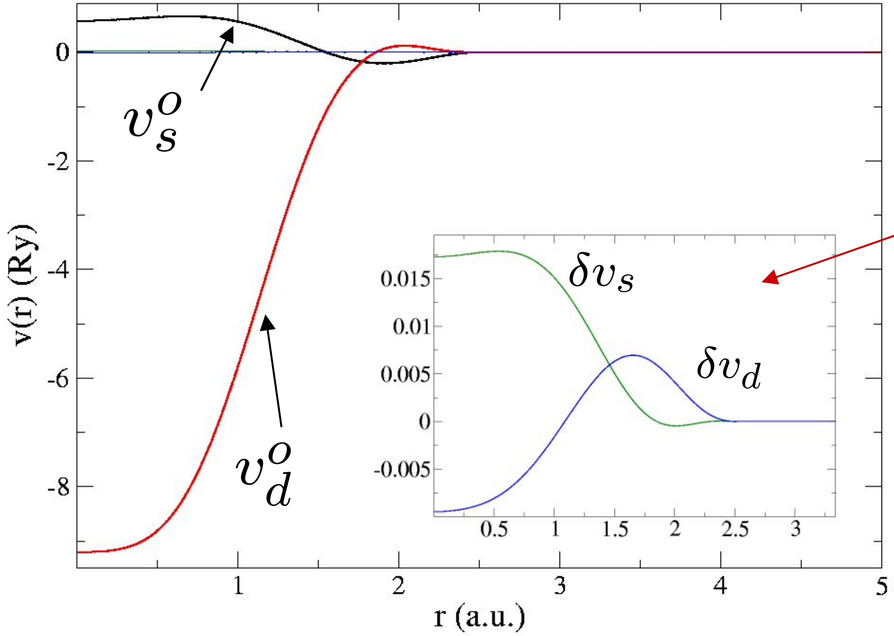
$$\beta(r) = \frac{n^{\uparrow}(r) - n^{\downarrow}(r)}{n^{\uparrow}(r) + n^{\downarrow}(r)}$$

S.C. Watson and E.A. Carter, PRB 58, R13309 (1998)

Spin-Dependent PsP theory

With $F\,[\beta(r)] \equiv \beta(r)$

$$\begin{cases} \dfrac{\delta E^{\text{ion}}}{\delta n^{\uparrow}(r)} = v^{o}(r) + \beta(r)\ [2-\beta(r)]\ \delta v(r) \\ \dfrac{\delta E^{\text{ion}}}{\delta n^{\downarrow}(r)} = v^{o}(r) - \beta(r)\ [2+\beta(r)]\ \delta v(r) \end{cases}$$



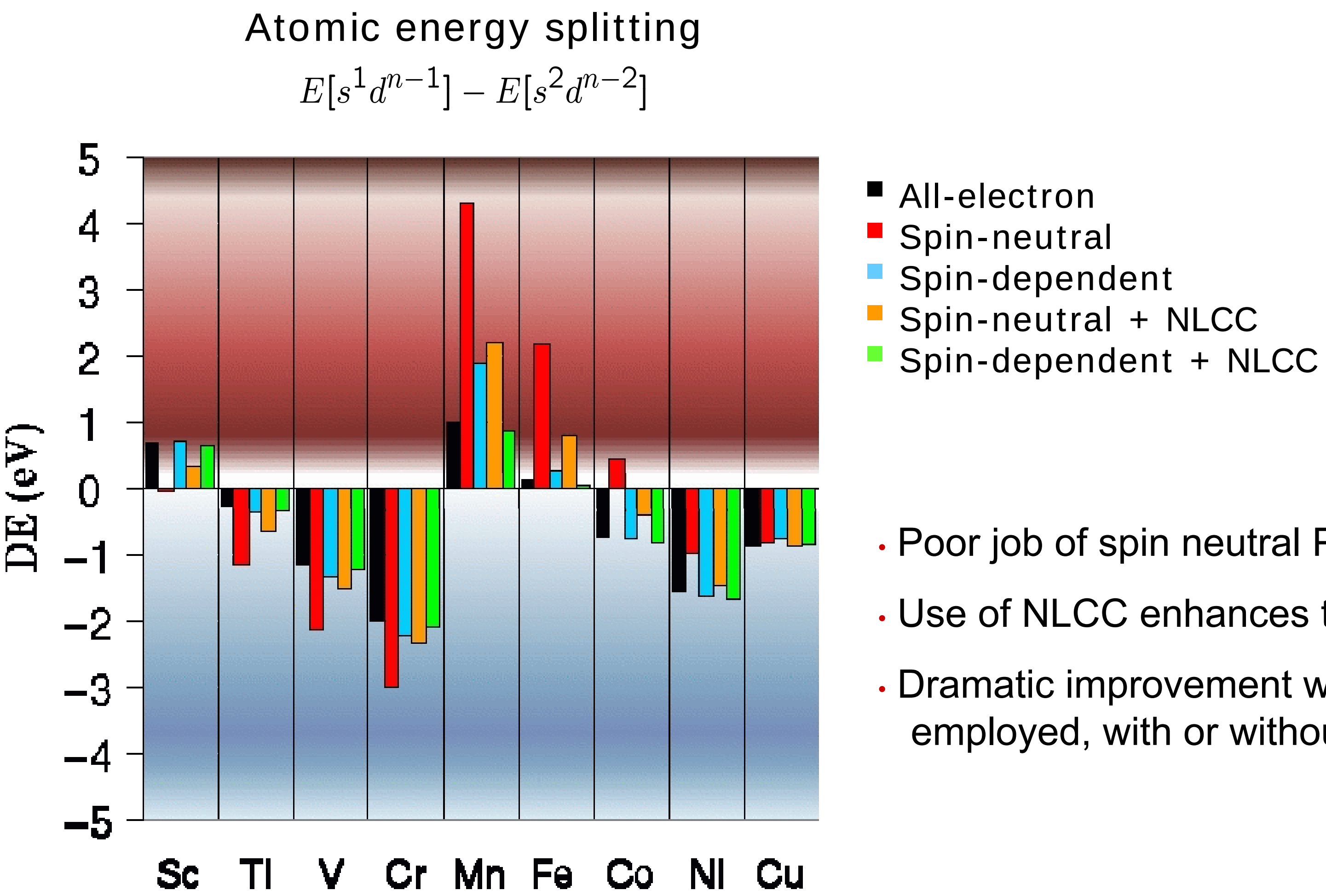
$$\delta v(r) = \frac{v^{\text{fp}}(r) - v^{o}(r)}{\beta_{\text{at}}(r)[2-\beta_{\text{at}}(r)]}$$

v^{O} Spin neutral reference atom

v^{fp} Fully polarized atom

- self-adaptive: atom & environment dependent
- allows for self-polarization in response to local spin polarization

SD-PsP atomic results


Atomic energy splitting

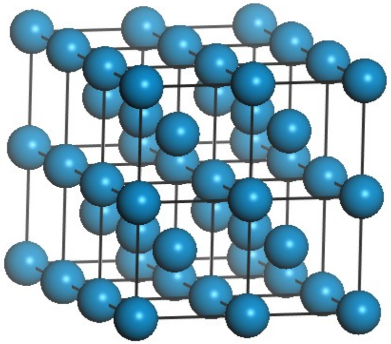
$E[s^1d^{n-1}] - E[s^2d^{n-2}]$

- Poor job of spin neutral PsP
- Use of NLCC enhances transferability
- Dramatic improvement when SD-PsP employed, with or without NLCC

S.C. Watson and E.A. Carter, PRB 58, R13309 (1998)

LDA Bulk properties: Ni & Fe

	a_o (Å)	B_o (GPa)	M (μb)
AE	3.42	254	0.62
SN-PsP	3.51	227	0.78
SD-PsP	3.50	240	0.57
Exp.	*3.52*	*184*	*0.62*



- Bulk fcc Ni
  - improved structural properties
  - accurate description of magnetism

	NLCC	a_o (Å)	B_o (GPa)	M (μb)
AE		2.75	250	1.98
SN-PsP	no	2.97	127	3.13
SD-PsP	no	2.81	254	2.00
SN-PsP	yes	2.83	229	2.15
SD-PsP	yes	2.83	240	2.13
Exp.		*2.87*	*167*	*2.20*

- Bulk bcc Fe
  - dramatic improvement due to spin-dependence
  - less when NLCC used (perturbation quenching)

Starrost *et al.*, PRB 64, 235105 (2001)

Cocula *et al.*, JCP 119, 7659 (2003)

Vanadium (001) surface magnetism

Experimentally

- Vanadium: paramagnetic metal in bulk, but magnetism not clear for surface
- V(001) films nonmagnetic on Ag substrate *(magneto-optic Kerr effect)*
- Induced magnetic order in V(001) ultra-thin films on Fe(001) *(EEL spectroscopy)*

Theoretically

- May exhibit magnetic ordering by loss of coordination

LDA-DFT

- Large surface magnetization (failure of the LDA?)

GGA-DFT

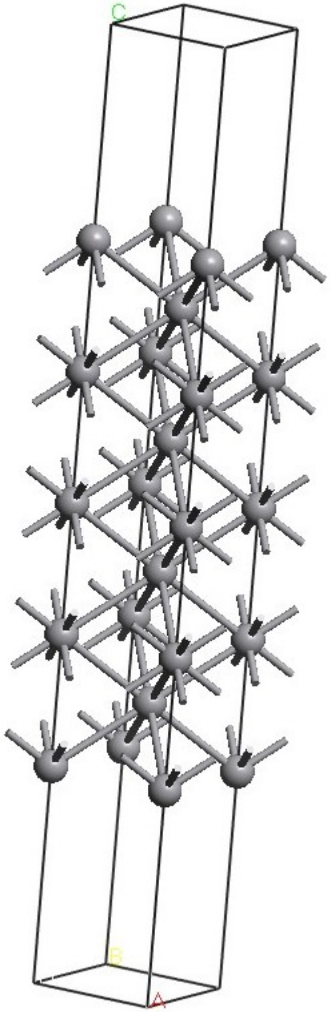
  - AE : small / no magnetization
  - PsPs : large magnetization

Breakdown of pseudopotential theory
Can our improved theory solve this ?

Computational details / Benchmarking

GOAL

- Examine discrepancies among PsPs results
- Can our SD-PsP succeed where others failed



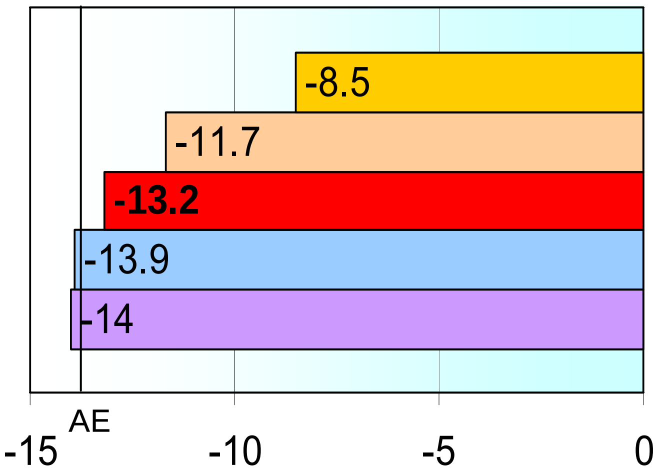
- 9-layer V(001) slab
- Exchange-correlation: GGA
- NLCC used
- Benchmarking on non-magnetic bulk bcc V

Method	a_o (Å)	B_o (GPa)
Exp.	*3.03*	*162*
AE	2.99	201
PsP	3.05	195
SN-PsP	3.05	197

Effect of PsP Parameters on V(001) surface properties

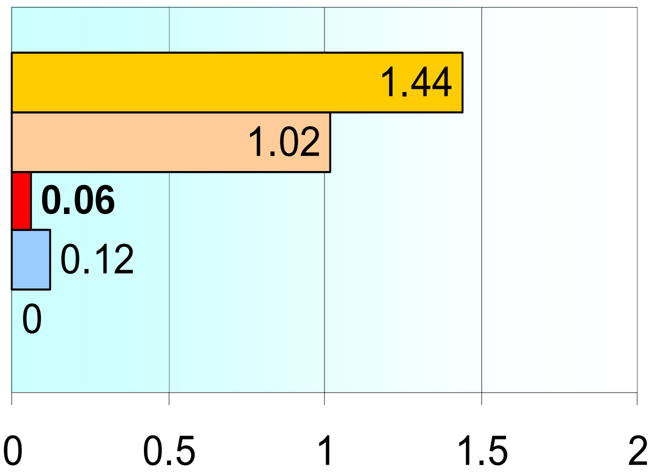
AE results: Δ_{12} = -13.7 % and M_s = 0.00 μ_b

SPIN-DEPENDENT PSEUDOPOTENTIAL IN RED



Surface layer inward relaxation (%)

r_d (Å)	r^{NLCC} (Å)
1.35	0.95
1.10	1.00
1.10	**1.00**
1.05	0.35
0.60	0.35



Surface magnetic moment (bohr)

- Larger cutoffs / softer PsP's: large errors in structural and magnetic properties
- Shorter cutoffs / harder PsP's: improved accuracy, at greater expense
- SD-PsP's: in good agreement with AE results *even with relatively large cutoff values*

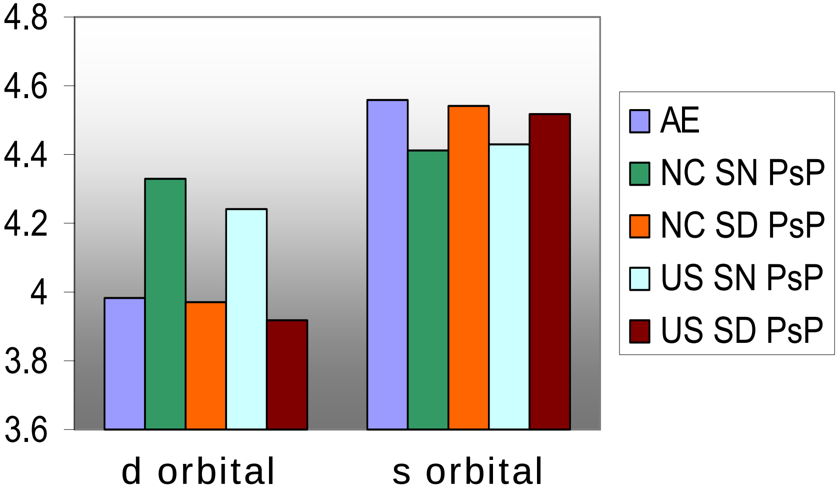
V. Cocula and E. A. Carter, *Phys. Rev. B*, **69**, 052404 (2004).

Ultrasoft SD-PsP

GOAL

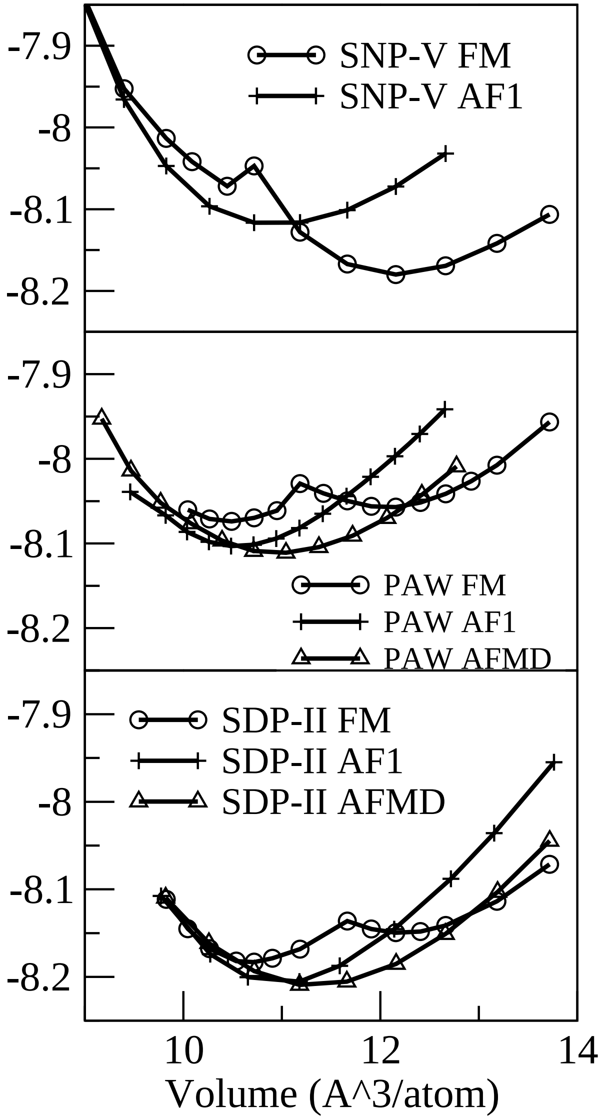
- Accuracy of spin-dependent PsPs
- Advantageous computational cost of ultrasoft PsPs

LDA
Atomic Cr orbital energies (eV)
$3d^{5\uparrow,0\downarrow}4s^{1\uparrow,0\downarrow}$

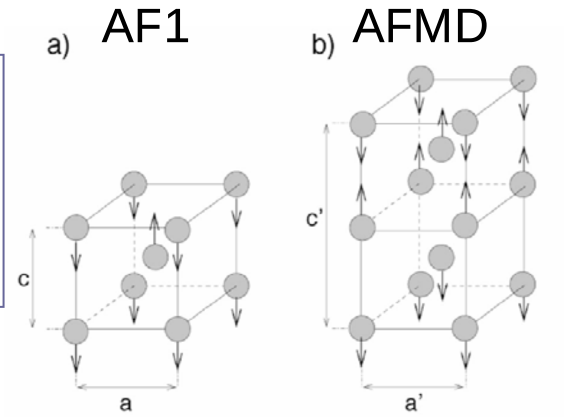


What we can hope for:

- Accurate ultrasoft PsPs even with large cutoff parameters
- Inexpensive first-principles calculations
- Allows for accurate description of large-scale magnetic effects



Experimentally, fcc Fe is antiferromagnetic (AF), while ground state bcc Fe is ferromagnetic...



- AE PAW agrees with experiment, and predicts that, of the FM states, low-spin, small volume state preferred.
- SN-USPP qualitatively fails:
  - predicts FM more stable than AF
  - predicts high-spin, large volume FM more stable

SD-USPP reproduces AE calculations very well, showing how accuracy can be maintained with the reduced expense of the USPPs.

V.Cocula, C. Pickard, and EAC, PRB, submitted (2005)

Conclusions and Outlook

Transition elements are challenging for PsP theories

- US-PsP’s provide softer potentials but do not address the transferability problem
- NLCC necessary but not sufficient and somewhat ‘arbitrary’
- in all instances, accuracy is expensive

Spin-dependent pseudopotentials

- multi-reference – perturbation-like approach
- self-adaptable / more transferable
- can achieve accuracy using potentials with larger cutoffs
- Ultrasoft formalism: accurate and inexpensive

Applications in the near future

- V, Cr thin films on Fe substrates: competition between anti-ferro- and ferro-magnetism

Future for Condensed Matter DFT

- Long-range dispersion (van der Waals) forces
  van der Waals density functionals
  D.C. Langreth, Rutgers University
  B.I. Lundqvist, Chalmers University of Technology and Goteborg University

- Strongly correlated electrons
  Dynamical mean-field theory
  G. Kotliar, Rutgers University

- Excited states
  GW Method (delocalized excited states)
  S. Louie, UC Berkeley
  CI in DFT Embedding Theory
  E. A. Carter, Princeton
  Time-dependent DFT (localized excited states)
  E.K.U. Gross, Freie Universitat Berlin
  M. Casida, Université Joseph Fourier (Grenoble I)

- Linear scaling DFT (localized basis sets or orbital-free DFT)
  Goedecker Rev. Mod. Phys. 1999 and those cited therein…
  Wang & Teter, Perrot, Madden, Carter, Weeks