

Smooth interpolation in the periodic table

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What we want to do

- ▶ Given a geometry such as a crystal structure, find the chemical composition that gives the optimal properties in some sense.
- ▶ Might be related to cohesive energies, band gaps, ...

How we want to do it

- ▶ Find a way in which to interpolate smoothly between types of atom, i.e. we might have an atom which is 40% nitrogen and 60% ruthenium, or one which is vaguely reminiscent of plutonium, etc.
- ▶ Adjust the composition smoothly in such a way as to optimize the property of interest, and make the composition converge to something which actually exists.
- ▶ Each atom can be represented by a smoothly variable **pseudopotential**

The problem with atoms in calculations

Consider the Kohn-Sham equations

$$\left[\hat{T} + v \right] |\psi_n\rangle = \epsilon_n |\psi_n\rangle$$

with potential being the Hartree (Coulomb) potential of the charge distribution plus the exchange-correlation potential:

$$v = v_{\text{Ha}} + v_{\text{xc}}$$

- ▶ Atoms possess valence electrons, which are interesting
- ▶ They also possess strongly bound core electrons, which are not
- ▶ Electronic wave functions oscillate quickly near atoms, requiring very expensive high-resolution grids to represent them, particularly for core electrons
- ▶ We want a way to get rid of the oscillations and core electrons in calculations without changing the results

Pseudopotentials

- ▶ Merge core electrons with atomic nucleus to form “fuzzy” central charge distribution, and treat only the valence electrons explicitly
- ▶ Add a “potential” around each atom to eliminate oscillating behaviour in a controlled manner, without changing the atomic orbitals far away from the atom.
- ▶ In Kleiman-Bylander form, this atomic potential includes a local and a non-local part. For atom a ,

$$v^a = v_{\text{local}}^a + \sum_{ij} |p_i^a\rangle h_{ij}^a \langle p_j^a|$$

- ▶ Thus, the full potential is

$$v = v_{\text{Ha}} + v_{\text{xc}} + \sum_a v^a$$

Different Carbon pseudopotentials

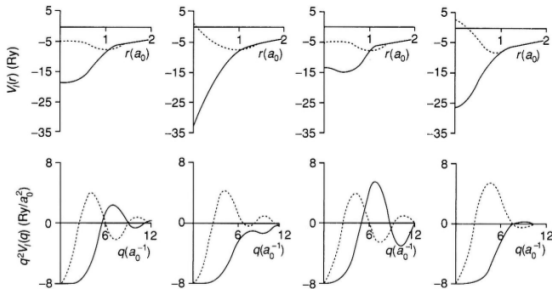
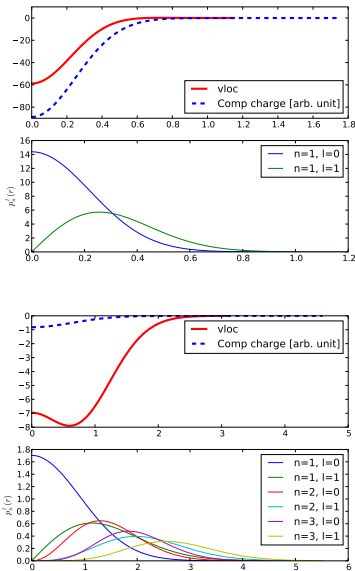


Figure 11.5. Comparison of pseudopotentials for carbon (dotted line for s and solid line for p) in real space and reciprocal space, illustrating the large variations in potentials that are all norm-conserving and have the same phase shifts at the chosen energies. In order from left to right generated using the procedures of: Troullier and Martins [502]; Kerker [501]; Hamann, Schlüter, and Chiang [471]; Vanderbilt [500]. From Troullier and Martins [502].

HGH pseudopotentials

- ▶ Hartwigsen, Goedecker, Hutter. Phys. Rev. B **58**, 3641, 1998.
- ▶ Local potential and projectors given analytically in terms of Gaussians and polynomials
- ▶ Each atomic species is represented by around 5-20 parameters
- ▶ Parameters are determined by requiring pseudoatoms to have correct eigenvalues
- ▶ Right: potentials/projectors for O, Au



Pseudopotential parameters

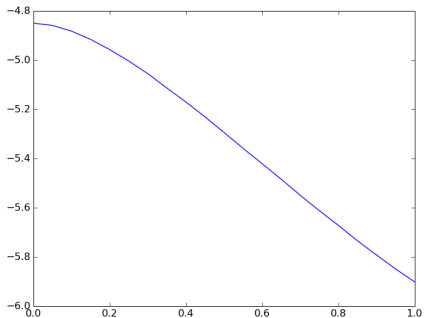
- ▶ The pseudopotential parameters are: widths of Gaussians and coefficients of polynomials in analytic forms of projectors and potential
- ▶ The atomic Hamiltonians h_{ij} , i.e. the coefficients with which the projectors enter in the total Hamiltonian

How to interpolate two pseudopotentials

- ▶ Take the weighted average of every above mentioned variable.
- ▶ (That might not be the best way, but we don't know that yet)

Mixing GaAs to SiSi

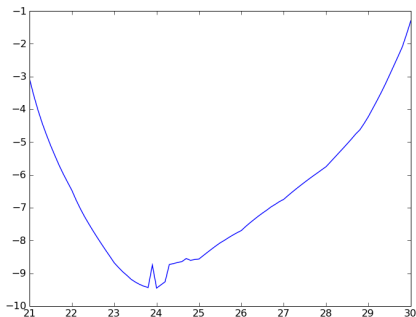
- ▶ Diamond structure with elements X and Y, where X morphs from Ga to Si while Y morphs from As to Si.
- ▶ Smooth - good for algorithms that depend on gradients



Cohesive energy [eV] as a function of mixture weight

Mixing Sc through Zn

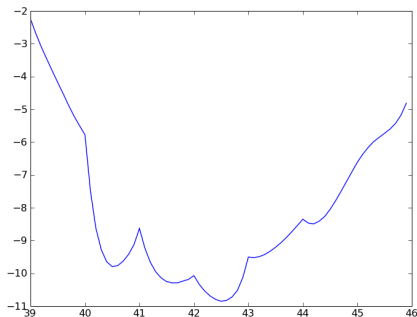
- ▶ Cohesive energy (almost) as a function of Z . Integers correspond to pure atoms, points in between are mixtures of neighbours
- ▶ (Irregular behaviour in the bottom is probably due to too high fermi smearing to get calculation to converge)



Approx. cohesive energy [eV] as a function of Z

Mixing Y through Cd

- ▶ Yuck!!
- ▶ The pseudopotentials are very unlike for these elements: large changes in local potential, different projector counts, ...
- ▶ Maybe we can make our own which have the same projector counts and do not need very different local potentials



Approx. cohesive energy [eV] as a function of Z

To do

- ▶ Understand mixing better (are the dips in energy due to ghost states?)
- ▶ Maybe construct more similar (and thus mixable) but equivalent pseudopotentials
- ▶ Maybe the mixing metric should be different, i.e. not just a linearly weighted average of all parameters
- ▶ Calculate analytical derivatives of the properties that are optimized, so gradient-based algorithms can search the periodic table