

In This Lecture:

➤ Pseudopotentials

Based on the References:

F. Nogueira , A. Castro, and M.A.L. Marques, 'A tutorial on density functional theory', (unpublished).
M. Fuchs and M. Scheffler, Computer Physics Communications, **119**, 67 (1999).

Pseudopotentials in Brief

- The electrons in the inner shells are strongly bound; they do not play a significant role in electronic & optical properties thus forming an almost inert core together with nucleus.
- The use of an effective interaction (pseudopotential) that represents the potential felt by the valence e's was first proposed by Fermi in 1934.
- Hellmann in 1935 suggested the form $w(r) = -\frac{1}{r} + \frac{2.74}{r} e^{-1.16r}$ for the potential felt by the single valence e of potassium (K).
- Pseudopotentials were ignored afterwards until late 1950's...
- In 1959 Phillips and Kleinman offered a more formal approach. They discriminated between the inner core and $|\psi_c\rangle$ valence states $|\psi_v\rangle$ and expressed the latter as

$$|\psi_v\rangle = |\varphi_v\rangle + \underbrace{\sum_c \alpha_{cv} |\psi_c\rangle}_{\text{oscillatory part that results from the orthogonalization of the } v \text{ to } c \text{ orbitals}}, \quad \alpha_{cv} = -\langle \psi_c | \varphi_v \rangle$$

smooth
pseudo-wf

oscillatory part that results from the
orthogonalization of the v to c orbitals

Acting on the smooth pseudo-wave function with the xtal Hamiltonian

$$\hat{H}|\varphi_v\rangle = E_v|\varphi_v\rangle + \sum_c (E_c - E_v)|\psi_c\rangle\langle\psi_c|\varphi_v\rangle$$

Observe that the pseudo-wave function states $|\varphi_v\rangle$ satisfy a Schrödinger-like equation with an energy-dependent pseudo-Hamiltonian:

$$\hat{H}^{\text{PK}}(E) = \hat{H} - \sum_c (E_c - E)|\psi_c\rangle\langle\psi_c|$$

So, we introduce the Philips-Kleinman pseudopotential as the term

$$\hat{w}^{\text{PK}}(E) = \hat{v} - \underbrace{\sum_c (E_c - E)|\psi_c\rangle\langle\psi_c|}_{\text{non-local part that also depends on the energy eigenvalue to be det'd}},$$

true
potential

non-local part that also depends
on the energy eigenvalue to be det'd

- The valence e 's feel an effective potential which is the result of the screening of the nuclear potential by the core e 's, the Pauli repulsion and xc effects bet. the v and c e 's. The non-local term in the previous psp equation represents then a repulsive potential making the psp much weaker than the true potential in the vicinity of the core. This is the so-called **Phillips-Kleinman Cancellation Theorem**.
- This implies that the pseudo-wf's will be smooth and will not oscillate in the core region. **Hence we can represent them with relatively few Fourier terms (RLVs)**.
- However, note that even though we deal with pseudo-potentials and pseudo-wf's, the energy eigenvalue is the **true energy** corresponding to the true wf.
- But, we use the pseudo-wf's in the subsequent computation of certain quantum processes (such as transition rates, etc.). This requires some caution!

Non-local PP's...

The pseudopotentials can be put into a form that emphasizes the angular momentum dependence:

$$w(\mathbf{r}, \mathbf{r}') = \sum_l \sum_{m=-l}^l Y_{lm}^*(\hat{r}) w_l(r, r') Y_{lm}(\hat{r}') ,$$

Spherical
Harmonics

Two special forms of practical importance:

1. Kleinman-Bylander separable form: $w_l(r, r') = v_l(r)v_l(r') ,$
2. Semi-local form: $w_l(r, r') = w_l(r)\delta(r - r') .$

However, the angular parts are still non-local

Ab-initio PP's...

Topp & Hopfield in 1973 suggested that the pseudopotentials should be adjusted such that they describe the valence charge density accurately.

Modern pseudopotentials are obtained by:

- Inverting the free atom Schrödinger equation for a given reference configuration
- Forcing the pseudo-wfs to coincide with the true (all-e) valence wfs beyond a certain distance, $r_c = r_l$
- The pseudo-wf should have the same norm as the valence wfs

These conditions can be written as:

$$R_l^{\text{PP}}(r) = R_{nl}^{\text{AE}}(r) \quad , \text{ if } r > r_l$$

$$\int_0^{r_l} dr |R_l^{\text{PP}}(r)|^2 r^2 = \int_0^{r_l} dr |R_{nl}^{\text{AE}}(r)|^2 r^2 \quad , \text{ if } r < r_l \quad ,$$

note the ang.mom.
dependence

r_l

And obviously we require the pseudo and true energy eigenvalues to coincide:

$$\varepsilon_l^{\text{PP}} = \varepsilon_{nl}^{\text{AE}}$$

The pseudopotentials constructed in this way are called **norm-conserving**. [A recent advancement is the so-called **ultrasoft pseudopotentials** developed by Vanderbilt in 90's which require small # plane waves ~20 Ry].

Quality of Pseudopotentials:

The cutoff radii, r_l can be considered as a measure of the quality of the PP. Their smallest value is determined by the location of the outermost nodal surface of the true wfs. For cutoff radii close to this minimum, the PP is very realistic but also very strong (too many plane waves). If very large cutoff radii are chosen, the PP will be smooth (less # plane waves) and almost angular momentum independent, but also very unrealistic.

More technicalities...

Relativistic effects, which in principle require a four-current Dirac-spinor formulation, are treated by using a scalar-relativistic kinetic energy operator. This takes into account the kinematic relativistic terms (the mass-velocity and Darwin terms) needed to properly describe the core states and the relativistic shifts of the valence levels, in particular for the heavier elements. The spin-orbit coupling terms are averaged over, as is commonly done in most cases.

The radial wfs u_{nl} are then the self-consistent eigenfn's of the scalar relativistic Schrödinger equation (in atomic units):

$$\left[\frac{1}{2M(r)} \left(-\frac{d^2}{dr^2} - \frac{1}{2M(r)c^2} \frac{dV(r)}{dr} r \frac{d}{dr} \frac{1}{r} + \frac{\ell(\ell+1)}{r^2} \right) + V(r) - \epsilon_l \right] u_{nl}(\epsilon_l, r) = 0,$$

where the relativistic e mass is $M(r) = 1 + \frac{\epsilon_l - V(r)}{2c^2}$

More technicalities...

Transferability of PP: Proper performance in different chemical environments. The pseudo atom transferability is checked for its scattering properties, excitation energies and chemical hardness properties in comparison to all-e atom.

Ghost states: For the commonly used fully separable Kleinman-Bylander form of PP it is important to rule out unphysical bound states or resonances appearing in the valence spectrum.

Nonlinear core-valence exchange correlation (NL cv XC) terms: Ordinary PP does not contain the NL cv XC terms such as $(n_c + n_v)^{4/3}$. These effects need to be included for “soft” valence shells (alkali’s), extended core states (Zn, Cd, ...), and in spin-density functional calculations.

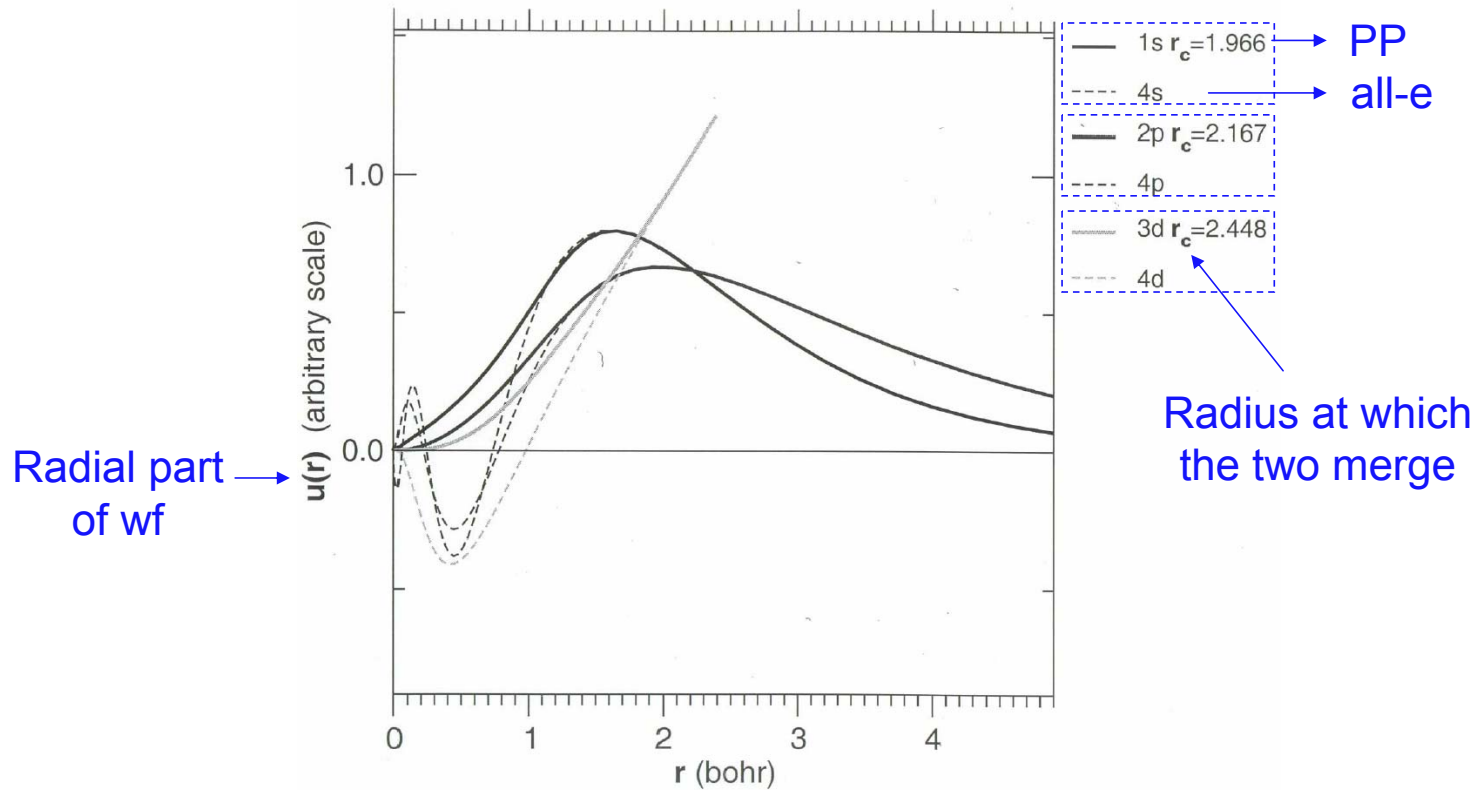
PAW: Projector Augmented Wave

- The PAW method, developed by Blöchl ('94) is a very powerful tool for performing pseudopotential electronic structure calculations within DFT, while retaining information about the correct nodal behavior of the valence electron wfs and has the ability to include upper core states in addition to valence states in the self-consistent iterations without significant additional computation.
- The problem of constructing the projector and basis functions needed for PAW technique is very similar to the problem of constructing local and nonlocal PPs.
- The method starts with a self-consistent all-e atomic structure calculation within the framework of DFT. The projector and basis functions are derived from the eigenstates of the all-e atomic Hamiltonian. They are determined iteratively solving radial differential equations.

For further PAW info, see for instance PRB 55, 2005 (1997).

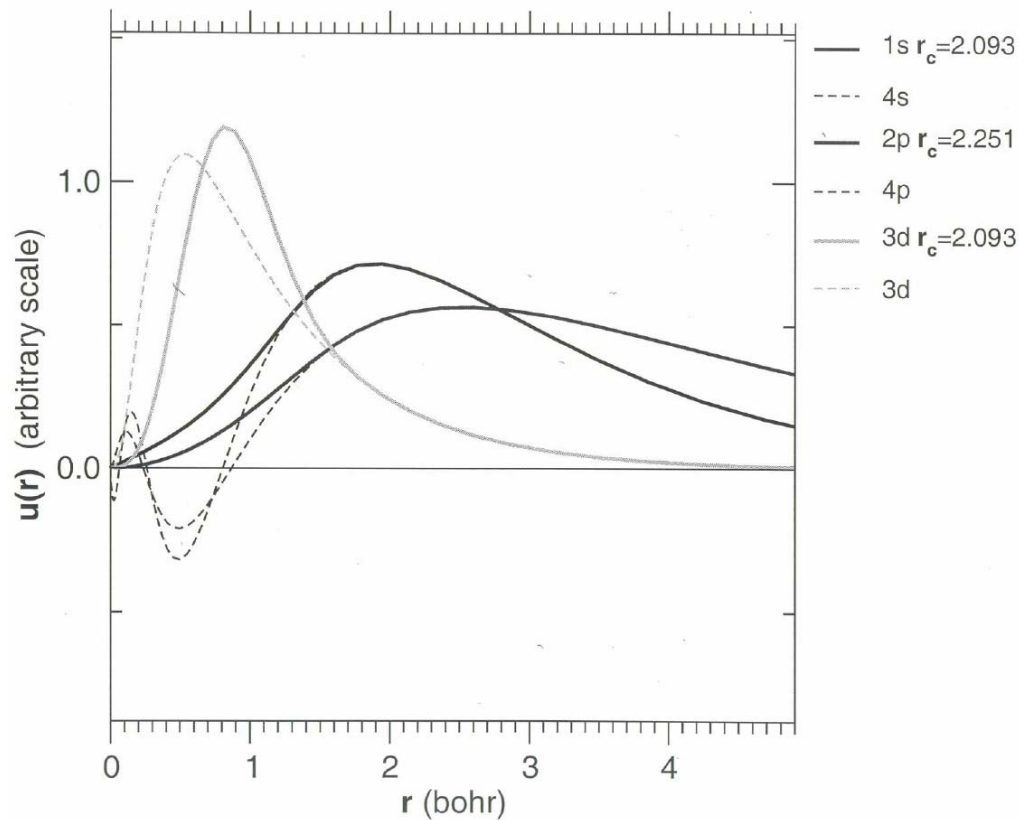
Comparison between all-e (true) and PP-wf's

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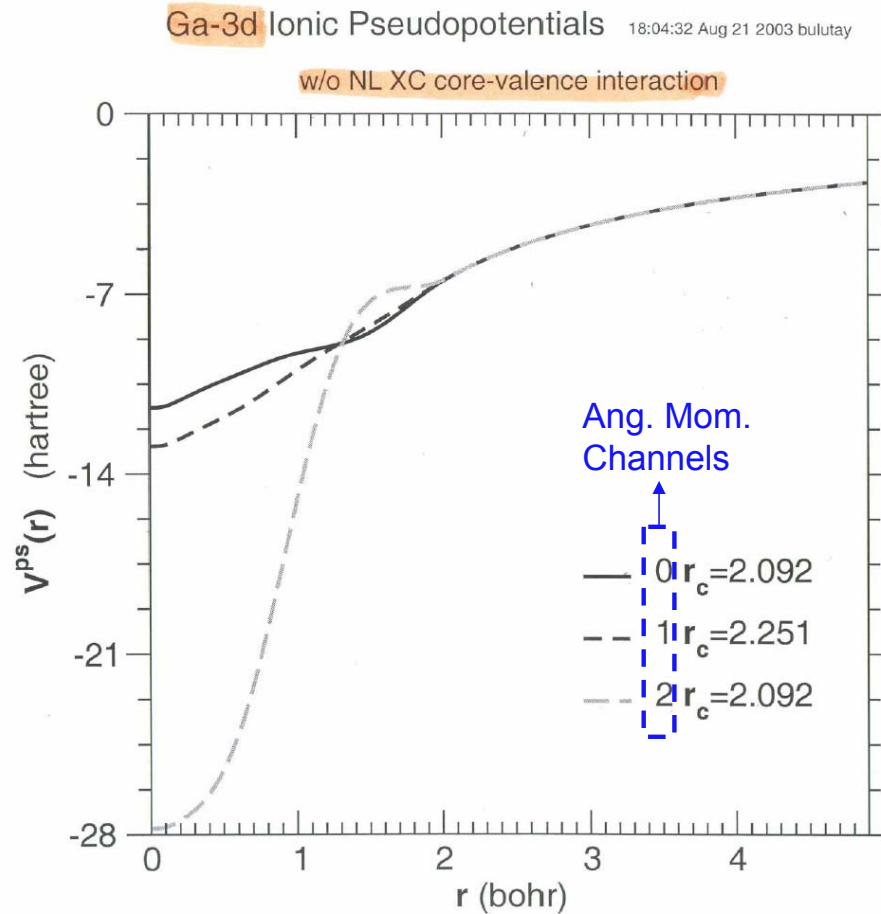


Comparison between true and PP-wf's

Ga-3d Pseudo vs All-Electron Wavefunctions 21:35:42 Aug 20 2003 bulutay



Non-local PP's for Ga with 3d



Non-local PP's for Ga with 3d & NL cv XC

