Pseudopotentials in Electronic Structure Theory

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OUTLINE

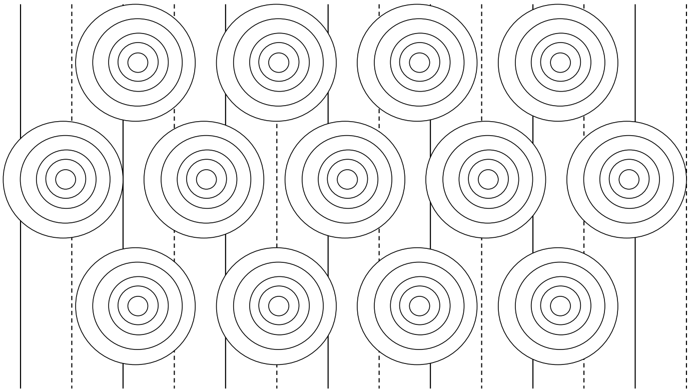
- Core States - inert but essential
- Methods that keep the core states: APW, LMTO
- Phase shifts for the scattering problem
- Replacing the cores by Pseudopotentials
- Norm-conserving pseudopotentials
- Soft pseudopotentials for k space calculations
- Generation of pseudopotentials in atomic calculations
- Fully separable "Kleinman-Bylander" pseudopotentials
- Other pseudopotentials

For more complete exposition and many references see
"Electronic Structure: Basic Theory and Practical Methods"
Richard M. Martin, Cambridge University Press, 2004
and
http://ElectronicStructure.org

Core States - essential, inert

- Highly localized around the nucleus
- Very large binding energies (dominate the total energies of most materials)
- High Fourier components - would require VERY large numbers of plane waves if done in plane wave calculations ($> 10^6$)
- Valence states must be orthogonal to core states - even MORE plane waves!

Figure 1: Schematic figure of crystal showing atomic-like core regions and regions between the atoms where the valence electronic states fare modified to form extended states of the crystal.



The APW method

- Slater, 1937
- Partition Space into sphere around each atom; interstitial region
- Define basis functions which are plane waves outside the spheres and augmented functions inside

  $$\psi_{\mathbf{k}} = \sum c_{\mathbf{G}} \psi^{APW}_{\mathbf{k}+\mathbf{G}}$$

  where

  $$\psi^{APW}_{\mathbf{K}} = e^{-i\mathbf{K}\cdot\mathbf{r}}$$

  outside the sphere. (Here $\mathbf{K} = \mathbf{k} + \mathbf{G}$).
- If the plane wave were continued inside the sphere its representation in spherical harmonics would be

  $$e^{-i\mathbf{K}\cdot\mathbf{r}} = 4\pi \sum_{lm} i^l j_l(Kr) Y_{lm} * (\theta_K, \phi_K) Y_{lm}(\theta, \phi)$$

- The real solution inside the sphere for a given l at the energy ε has a radial part $R_l(r, \varepsilon)$. Then we can construct

  $$\psi^{APW}_{\mathbf{K}} = 4\pi \sum_{lm} \frac{j_l(KR_s)}{R_l(R_s, \varepsilon)} i^l R_l(r, \varepsilon) Y_{lm} * (\theta_K, \phi_K) Y_{lm}(\theta, \phi)$$

  inside the sphere

APW continued

- The APW function so constructed is continuous (but not the derivative) and is an APW basis function.
- Since $R_l(r, \varepsilon)$ satisfies the Schrödinger Eq. inside the sphere, any combination of the APW's satisfies the equation.
- A small number of APW's is sufficient to represent the real wavefunction, and the secular equation can be written

$$det||(\frac{1}{2}|\mathbf{k}+\mathbf{G}|^2 - \varepsilon)\delta_{\mathbf{G},\mathbf{G}'} + V^{APW}_{\mathbf{G},\mathbf{G}'}(\varepsilon)|| = 0.$$

- A small number of APW's is sufficient to represent the real wavefunction, and there is a small secular equation. The price is that the effective potential must be found as a function of the eigenvalue.

MTO is a muffin tin orbital, which matches the inner solution to a radial solution of the Helmholz equation instead of plane waves.

The OPW method

- Herring, 1940
- n OPW is a plane wave which is explicitly made orthogonal to a core state, treated as a known function (it is very similar to the atomic function)

  $$\psi^{OPW}_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = e^{-i\mathbf{G}\cdot\mathbf{r}} - \sum_c \beta_c \psi_c(\mathbf{r})$$

  or in schematic form

  $$\psi = \phi - \sum_c \langle \psi_c | \phi \rangle \phi$$

  which is explicitly orthogonal to each ψ_c.
- the secular equation can be written

  $$det||(\frac{1}{2}|\mathbf{k}+\mathbf{G}|^2 - \varepsilon)\delta_{\mathbf{G},\mathbf{G}'} + V^{OPW}_{\mathbf{G},\mathbf{G}'}(\varepsilon)|| = 0.$$

  where

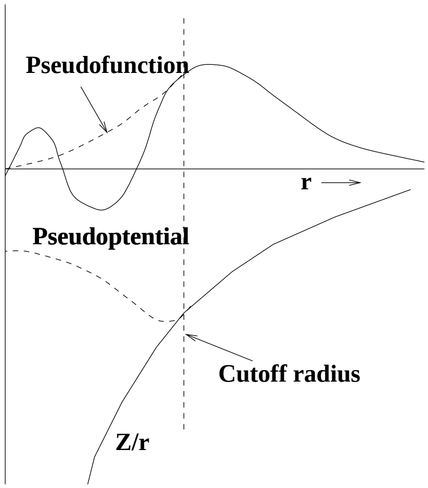
  $$V^{OPW} = V_{\mathbf{G},\mathbf{G}'} + \sum_c (\varepsilon - \varepsilon_c)|\psi_c\rangle\langle\psi_c|$$

  is a non-local potential operator.

Scattering and Pseudopotentials

- ANY wavefunction outside the spheres is given correctly if the scattering phase shifts at the sphere boundary are given correctly. (See, for example, Schiff)
- Define the phase shifts for each angular momentum, which are only *weakly* dependent on energy
- Choose a pseudopotential as *any* potential which does not have bound core states but gives the same same phase shifts at the valence state energies. Then it will give the same eigenvalues.
- Empirical pseudopotentials: Define potentials which give the desired bands. (Phillips and Kleinman, 1959).

Figure 2: Schematic figure of pseudopotential and pseudofunction. Since the functions depend upon angular momentum l, the potentials must also depend on l, i.e., they are *non-local*).



Norm-Conserving Pseudopotentials

"Norm-conserving" pseudopotentials (NCPP's) [Hamann, Schluter, Chiang] and "shape-consistent" [Krauss and Stevens] are the basis of most "ab initio" pseudopotentials used today. Norm-conservation has the obvious advantage that the usual normalized functions are defined to have the correct amount of charge inside the core region. The added advantage (proved on the following page) is embodied in the relation of norm-conservation and the first log derivative of the phase shift with respect to the energy. This is important because the scattering properties of the pseudopotential are correct not only at a chosen reference energy but also over a range of energies. This leads to increased "transferability".

The key steps in construction of a NCPP are:

- Construct pseudopotential from an all-electron calculation on a atom
- Require the pseudopotential to:
  - equal the all-electron potential outside the sphere.
  - have eigenvalue equal the all-electron valence eigenvalue
  - have an eigenfunction whose norm inside the sphere is conserved
- Then the normalized function equals the all-electron function outside the sphere, the charge inside is the same. It follows that the potential outside the sphere is the same.
- And the first logarithmic derivative of the phase shift as a function of energy is the same as for the all-electron case. at the valence energy. This ensures maximum transferability to situations where the eigenvalue id changed.
- The resulting potential is l-dependent

$$V(\mathbf{r}, \mathbf{r}') = \sum_{lm} V_l(r)\delta(r - r')Y_{lm}(\theta, \phi)Y_{lm}(\theta', \phi')$$

Norm-Conserving Pseudopotentials

Norm-conservation and first energy derivative of phase shift

(Following the proof given by Shirley, et al. and summarized in the book by Martin.)

A NCPP is equal the all-electron potential outside a "core region" of radius R_c; inside R_c the potential is chosen to give the desired eigenvalue and norm. Then $\psi_{l,m} = r^{-1}\phi(r)P_l(cos(\theta))exp(im\phi)$ that satisfies the norm-conservation condition,

$$Q = \int_0^{R_c} d^3\mathbf{r}\psi|\mathbf{r}|^2 = \int_0^{R_c} dr\phi\left(r\right)^2, \tag{1}$$

where Q is the same for the all-eelctron radial orbital ϕ and the pseudo radial orbital ϕ^{PS}. This insures that a normalized ϕ^{PS} will equal ϕ for $r \geq R_c$, and the total charge in the core region is correct.

The radial Schrödinger equation at energy E, which need not be an eigenenergy. is

$$\frac{-\hbar^2}{2m_e}\frac{d^2}{dr^2}\phi(r) + (\frac{l(l+1)}{2r^2} + V(r) - E)\phi(r) = 0. \tag{2}$$

In terms of the logarithmic derivative $x(r) = \phi'(r)/\phi(r)$, this can be written

$$x'(r) + [x(r)]^2 = \frac{l(l+1)}{r^2} + 2(V(r) - E)$$

Using the relation valid for any function, $f'(r) + 2x(r)f(r) = \frac{1}{\phi(r)^2}\frac{d}{dr}[\phi(r)^2 f(r)]$, differentiating the equation for x(r) with respect to E, multiplying by $\phi(r)^2$ and integrating, one finds

$$\frac{\partial x(R)}{\partial E} = \frac{1}{\phi\left(R\right)^2}\int_0^R dr\phi\left(r\right)^2 = \frac{1}{\phi\left(R\right)^2}Q(R). \tag{3}$$

This shows immediately that norm-conservation implies that the first energy derivative of $x(R)$ is also correct. Since $\phi^{PS} = \phi$ for $r \geq R_c$, at the chosen energy, the change in $\phi^{PS}(r)$ for $r \geq R_c$ is given correctly to first order in a change in the energy.

Separable Pseudopotentials

- Kleinman-Bylander, 1982
- Form similar to OPW non-local operator form, but taking advantage of the arbitrariness to create smooth projection operators which lead to the same phase shifts
- $$V_{KB}(\mathbf{r},\mathbf{r}') = V_{KB}^{local}(r)\delta(\mathbf{r}-\mathbf{r}') + \delta V_{KB}(\mathbf{r},\mathbf{r}')$$
- In operator notation the non-local part is

  $$\delta V_{KB}(\mathbf{r},\mathbf{r}') = \sum_{lm} \frac{|\delta V_l \phi_{lm}\rangle\langle\phi_{lm}\delta V_l|}{\langle\phi_{lm}|V_l|\phi_{lm}\rangle}$$

  where

  $$\phi_{lm}(\mathbf{r}) = R_l(r) Y_{lm}(\theta,\phi)$$
- Obviously gives same answer as ordinary pseudopotential for atom
- Form similar to OPW non-local operator form, but taking advantage of the arbitrariness to create smooth projection operators which lead to the same phase shifts
- Can be improved by adding more projection functions
- Works well is solids, molecules. Efficient.
- Potential problem. ”Ghost states” can occur. Can be avoided with care. Gonze, Stumpf, Scheffler, PRB 44, 9503 (1991).

Other Recent forms

- Pseudohamiltonians - Bachelet, Ciochetti, Ceperley
  - Modify the mass term inside the sphere
  - Not as general and accurate as the norm-conserving potentials, but very useful for Diffusion Monte Carlo
- Vanderbilt "Ultrasoft" form
  - Define an auxiliary function added to the plane waves around each atom.
  - Allows fewer plane waves for a good description.
  - In spirit of OPW but with a smooth auxiliary function.

Useful web sites

- See links at

  `http://electronicstructure.org/`

  - Book information

    `http://electronicstructure.org/book.asp`

  - Links for Chapter 11, Pseudopotentials:

    `http://electronicstructure.org/book.asp#CH11-Pseudopotentials`

  - Links for Chapter 13, Plane waves II:

    `http://electronicstructure.org/book.asp#CH13-Planewaves-2`

- Web interface for generation of pseudopotentials in various formats at the TDDFT site "Octopus":

  `http://www.tddft.org/programs/octopus/pseudo.php`

- The Jos Lus Martins site:

  `http://bohr.inesc.pt/˜jlm/pseudo.html`

- David Vanderbilt's Ultrasoft site:

  `http://www.physics.rutgers.edu/˜dhv/uspp/`

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