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SMR/1310 - 6

**SPRING COLLEGE ON
NUMERICAL METHODS IN ELECTRONIC STRUCTURE THEORY**

(7 - 25 May 2001)

**"The plane-wave pseudo-potential method"
(PW - II)**

presented by:

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Outline of lesson 2:

- *norm-conserving* pseudopotentials from first principles (Hamann-Schlüter-Chiang)
- *separable* form of pseudopotentials (Kleinman-Bylander)
- extended non-periodic systems (defects in crystals, surfaces, alloys) and finite systems (molecules, clusters): *supercells*.
- (very) short introduction to *self consistency*

Norm-Conserving, DFT-based PPs were introduced by Hamann, Schlüter, Chiang in 1979. For a given reference atomic configuration, they must meet the following conditions:

- $\epsilon_l^{ps} = \epsilon_l^{ae}$
- $\phi_l^{ps}(r)$ is nodeless
- $\phi_l^{ps}(r) = \phi_l^{ae}(r)$ for $r > r_c$
- $\int_{r < r_c} |\phi_l^{ps}(r)|^2 r^2 dr = \int_{r < r_c} |\phi_l^{ae}(r)|^2 r^2 dr$

where $\phi_l^{ae}(r)$ is the radial part of the atomic valence wavefunction with l angular momentum, ϵ_l^{ae} its orbital energy. The *core radius* r_c is approximately at the outermost maximum of the wavefunction.

Features of Norm-conserving PPs:

- + *transferrable*: their construction ensures that they reproduce the logarithmic derivatives, i.e., the *scattering properties*, of the true potential in a wide range of energies. See the identity

$$-2\pi \left[(r\phi(r))^2 \frac{d}{d\epsilon} \left(\frac{d}{dr} \ln \phi(r) \right) \right]_{r_c} = 4\pi \int_0^{r_c} |\phi(r)|^2 r^2 dr$$

valid for any regular solution of the Schrödinger equation at energy ϵ .

- *non local*: there is one potential per angular momentum:

$$V^{ps}(\mathbf{r}) = \sum_l V_l(r) |l\rangle \langle l|.$$

Traditionally PPs are split into a *local* part, long-ranged and behaving like $-Z_v e^2 / r$ for $r \rightarrow \infty$, and a short-ranged *semilocal* term:

$$\hat{V}^{ps} = \hat{V}_{loc} + \hat{V}_{SL}, \quad \hat{V}_{loc} \equiv V_{loc}(r), \quad \hat{V}_{SL} \equiv \sum_{lm} V_l(r) \delta(r - r') Y_{lm}(\hat{\mathbf{r}}) Y_{lm}^*(\hat{\mathbf{r}}'),$$

where Y_{lm} = spherical harmonics, $\sum_{lm} = \sum_l \sum_{m=-l}^l$

Generation of norm-conserving PPs

1. From an all-electron self-consistent DFT calculation in an atom with a given reference configuration, calculate ϕ_l^{at} and ϵ_l^{at}
- 2a. Generate ϕ_l^{ps} for valence states that obey norm-conservation conditions, and invert the Kohn-Sham equation at ϵ_l^{ps} to get $V_l(r)$

or

- 2b. Generate $V_l(r)$ such that ϕ_l^{ps} and ϵ_l^{ps} obey norm-conservation conditions
3. *Unscreen* $V_l(r)$ by removing the valence contribution to Hartree and exchange-correlation potentials:

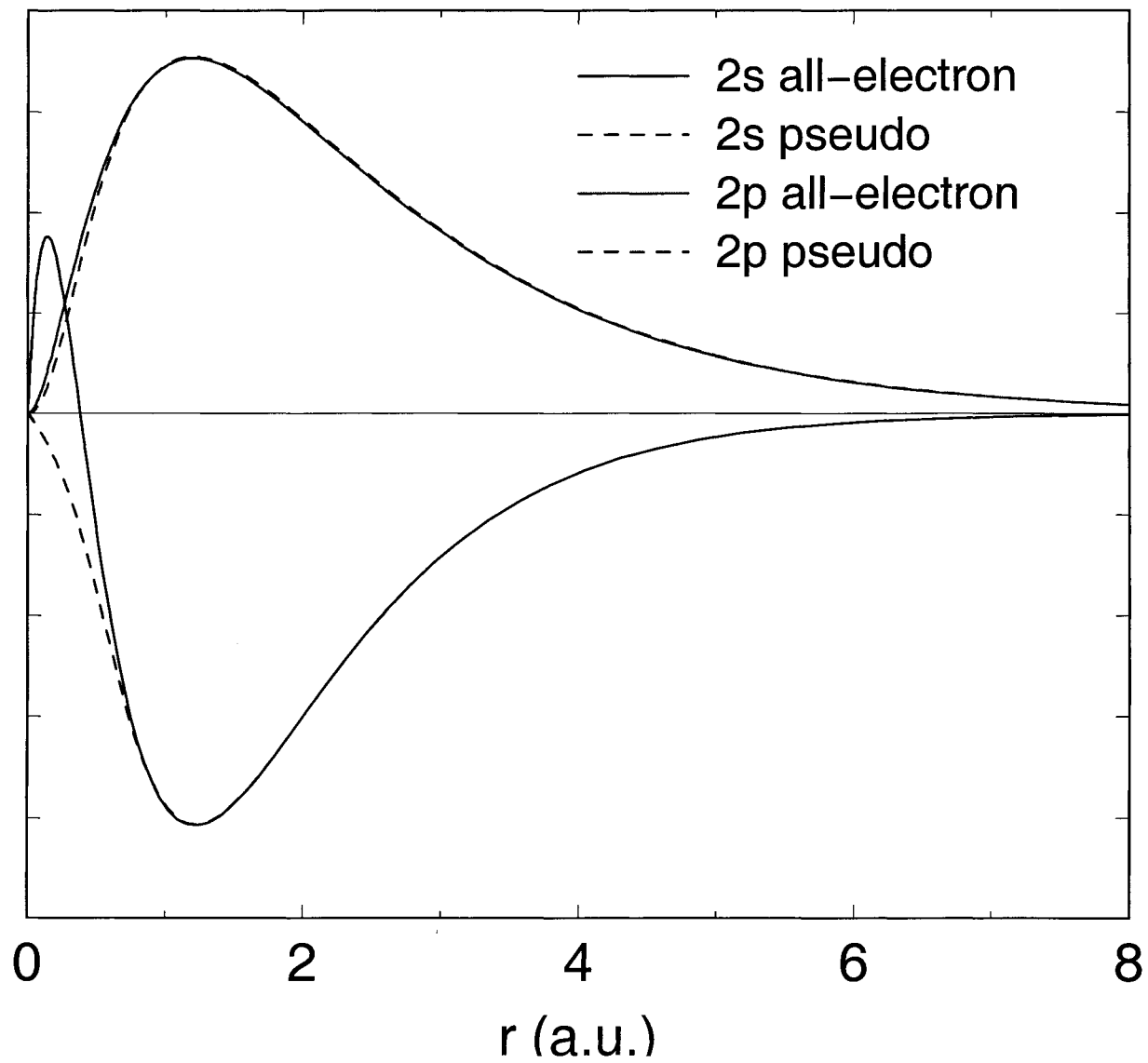
$$V_l^{ps}(r) = V_l(r) - V_H(n^{ps}(r)) - V_{xc}(n^{ps}(r))$$

where $n^{ps}(r)$ is the atomic valence charge density (assumed to be spherical):

$$n^{ps}(r) = \frac{1}{4\pi} \sum_l f_l |\phi_l^{ps}(r)|^2$$

(f_l is the occupancy of state with angular momentum l).

Carbon 2s² 2p²



Desirable characteristics of a PP:

- Transferability: can be estimated from atomic calculations on different configurations. In many cases simple unscreening produces an unacceptable loss of transferability. May require the *nonlinear core correction*:

$$V_l^{ps}(r) = V_l(r) - V_H(n^{ps}(r)) - V_{xc}(n_c(r) + n^{ps}(r))$$

where $n_c(r)$ is the core charge of the atom (Froyen, Louie, Cohen 1982)

- Softness: atoms with strongly oscillating pseudo-wavefunctions (first-row elements, elements with $3d$ and $4f$ valence electrons) will produce *hard* PPs requiring many PW in calculations. Larger core radius means better softness but worse transferability. Various recipes to get optimal smoothness without compromising transferability: Troullier and Martins (1990), Rappe Rabe Kaxiras Joannopoulos (1990)

Desirable characteristics of a PP (continued):

- Computational efficiency: Norm-conserving PPs are not ideal from this point of view. Matrix elements of the semilocal part are awkward:

$$\langle \mathbf{k} + \mathbf{G} | \hat{V}_{SL} | \mathbf{k} + \mathbf{G}' \rangle = \frac{1}{\Omega} \sum_{lm} \int e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} Y_{lm}(\hat{\mathbf{r}}) V_l(r) Y_{lm}^*(\hat{\mathbf{r}}') \delta(r - r') e^{i(\mathbf{k}+\mathbf{G}')\cdot\mathbf{r}'} d\mathbf{r} d\mathbf{r}'$$

(for one atom at $\mathbf{r} = 0$). Using the expansion of PWs into spherical Bessel functions j_l :

$$e^{i\mathbf{q}\cdot\mathbf{r}} = 4\pi \sum_l i^l j_l(qr) \sum_m Y_{lm}^*(\hat{\mathbf{q}}) Y_{lm}(\hat{\mathbf{r}})$$

one gets:

$$\langle \mathbf{k} + \mathbf{G} | \hat{V}_{SL} | \mathbf{k} + \mathbf{G}' \rangle = \frac{4\pi}{\Omega} \sum_l (2l + 1) P_l(\mathbf{k}_1 \cdot \mathbf{k}_2) \int r^2 j_l(k_1 r) V_l(r) j_l(k_2 r) dr$$

where $\mathbf{k}_1 = \mathbf{k} + \mathbf{G}$, $\mathbf{k}_2 = \mathbf{k} + \mathbf{G}'$, $P_l(x) =$ Legendre polynomials.

Separable (Kleinman-Bylander) form of PPs

$$\hat{V}^{ps} \rightarrow \hat{V}_{KB} = \hat{V}'_{loc} + \hat{V}_{NL}$$

where:

$$\hat{V}_{NL} \equiv \frac{|V'_l \phi_l^{ps}\rangle \langle V'_l \phi_l^{ps}|}{\langle \phi_l^{ps} | V'_l | \phi_l^{ps} \rangle},$$

$V'_l(r) = V_l(r) - V_0(r)$, $\hat{V}'_{loc} \equiv V_{loc}(r) + V_0(r)$, and $V_0(r)$ an arbitrary function. The ϕ_l^{ps} are the atomic pseudo-wavefunction for the reference state.

What is the logic behind this transformation ? On the reference state, $\hat{V}_{KB}|\phi_l^{ps}\rangle = \hat{V}^{ps}|\phi_l^{ps}\rangle$; on states not too far from the reference state, $\hat{V}_{KB}|\phi_l\rangle \simeq \hat{V}^{ps}|\phi_l\rangle$.

The KB separable form is an *approximation* if applied to a PP generated as shown before (but PPs can be *directly* produced in separable form: Vanderbilt 1991). It generally yields good results, but may badly fail in some cases due to the appearance of *ghost states*.

Separable PPs are computationally much more efficient than the conventional (semilocal) form. Matrix elements of the separable part:

$$\begin{aligned} \langle \mathbf{k} + \mathbf{G} | \hat{V}_{KB} | \mathbf{k} + \mathbf{G}' \rangle &= \frac{1}{\Omega} \sum_{lm} \frac{1}{\langle \phi_l^{ps} | V_l' | \phi_l^{ps} \rangle} \int e^{-i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}} V_l'(r) \phi_l^{ps}(r) Y_{lm}(\hat{\mathbf{r}}) d\mathbf{r} \\ &\times \int e^{i(\mathbf{k}+\mathbf{G}') \cdot \mathbf{r}'} V_l'(r') \phi_l^{ps}(r') Y_{lm}^*(\hat{\mathbf{r}}') d\mathbf{r}' \end{aligned}$$

(for one atom at $\mathbf{r} = 0$). Using the expansion of PW into spherical Bessel functions one gets:

$$\begin{aligned} \langle \mathbf{k} + \mathbf{G} | \hat{V}_{KB} | \mathbf{k} + \mathbf{G}' \rangle &= \frac{4\pi}{\Omega} \sum_{lm} \frac{1}{\langle \phi_l^{ps} | V_l' | \phi_l^{ps} \rangle} Y_{lm}(\hat{\mathbf{k}}_1) \int r^2 j_l(k_1 r) V_l'(r) \phi_l^{ps}(r) dr \\ &\times Y_{lm}^*(\hat{\mathbf{k}}_2) \int r^2 j_l(k_2 r) V_l'(r) \phi_l^{ps}(r) dr. \end{aligned}$$

Much faster and much less storage needed than with separable PPs.

What about non periodic systems ? e.g. defects in crystals, surfaces, alloys, amorphous materials, liquids, molecules, clusters?

Use **supercells**: introduce an artificial periodicity.

The supercell geometry is dictated by the type of system under investigation:

- Defects in crystals:
the supercell is commensurate with the perfect crystal cell. The distance between periodic replica of the defect must be “big enough” to minimize spurious defect-defect interactions.
- Surfaces:
slab geometry. The number of layers of the materials must be “big enough” to have “bulk behaviour” in the furthest layer from the surface. The number of empty layers must be “big enough” to have minimal interactions between layers in different regions.
- Alloys, amorphous materials, liquids:
the supercell must be “big enough” to give a reasonable description of physical properties.
- Molecules, clusters:
the supercell must allow a minimum distance of at least a few Å (~ 6) between the closest atoms in different periodic replica.

How to find the DFT ground state of a system ?

- Solving the Kohn-Sham equations self-consistently

$$(T + V + V_H(n) + V_{XC}(n))\psi_i = \epsilon_i\psi_i$$

with charge density $n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2$, $i \equiv \{\mathbf{k}, \text{band index}\}$, $f_i =$ occupancy of states, and orthonormality constraints $\langle \psi_i | \psi_j \rangle = \delta_{ij}$

- By constrained minimization of the energy functional

$$E[\{\psi_i\}] = \sum_i f_i \langle \psi_i | T + V | \psi_i \rangle + \frac{e^2}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{XC}(n) + E_{ion-ion}$$

with charge density and orthonormality constraints as above. Equivalently: minimize

$$E[\{\psi_i\}] - \Lambda_{ij} (\langle \psi_i | \psi_j \rangle - \delta_{ij})$$

where the Λ_{ij} are Lagrange multipliers