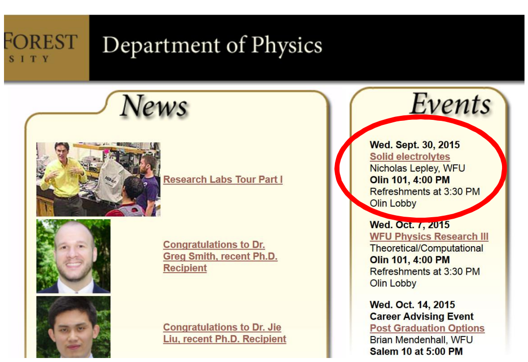
PHY 752 Solid State Physics
11-11:50 AM MWF Olin 103

Plan for Lecture 16:
Reading: Chapter 5 in GGGPP
Ingredients of electronic structure calculations

1. Plane wave basis sets
2. Construction of pseudopotentials
3. Projector Augmented Wave (PAW) method

4	Wed, 9/02/2015	Chap. 1.6, 2.1	Crystal structures	#4
5	Fri, 9/04/2015	Chap. 2	Group theory	#5
6	Mon, 9/07/2015	Chap. 2	Group theory	#6
7	Wed, 9/09/2015	Chap. 2	Group theory	#7
8	Fri, 9/11/2015	Chap. 2	Group theory	#7
9	Mon, 9/14/2015	Chap. 2.4-2.7	Densities of states	#8`
10	Wed, 9/16/2015	Chap. 3	Free electron model	#9
11	Fri, 9/18/2015	Chap. 4	One electron approximations to the many electron problem	#10
12	Mon, 9/21/2015	Chap. 4	One electron approximations to the many electron problem	#11
13	Wed, 9/23/2015	Chap. 4	Density functional theory	#12
14	Fri, 9/25/2015	Chap. 5	Implementation of density functional theory	#13
15	Mon, 9/28/2015	Chap. 5	Implementation of density functional theory	#14
16	Wed, 9/30/2015	Chap. 5	First principles pseudopotential methods	#15
17	Fri, 10/02/2015			
18	Mon, 10/05/2015			
19	Wed, 10/07/2015			
20	Fri, 10/09/2015			
	Mon, 10/12/2015		No class	Take-home exam
	Wed, 10/14/2015		No class	Take-home exam due
	Fri, 10/16/2015		Fall break -- no class	



WFU Physics Colloquium

TITLE: Investigating Li-ion solid electrolytes using simulations based on density functional theory

SPEAKER: Nicholas D. Lepley,

Department of physics,
Wake Forest University

TIME: Wednesday September 30, 2015 at 4:00 PM

PLACE: Room 101 Olin Physical Laboratory

Refreshments will be served at 3:30 PM in the Olin Lounge. All interested persons are cordially invited to attend.

ABSTRACT

Lithium ion batteries are used in a diverse array of applications. They power laptops and cellphones, houses and automobiles, airliners and Mars rovers. The success of Li-ion batteries has driven growing demand for batteries with higher capacity and longer lifetimes. One of the most promising paths to improving Li batteries is the development of solid electrolyte materials. This talk will briefly summarize some of my investigations of novel lithium phosphate and thiophosphate solid electrolytes, the computational quantum mechanics that enabled those investigations, as well as explaining how Li-ion batteries work and what we are doing to make them last longer.

Some practical considerations in electronic structure calculations

Bloch theorem

$$\Psi_{n\mathbf{k}}(\mathbf{r}+\mathbf{T}) = e^{i\mathbf{k}\cdot\mathbf{T}}\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$$

Plane wave representation

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n\mathbf{k}}(\mathbf{G})e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

In practice, summation is truncated:

$$\frac{\hbar^2|\mathbf{k}+\mathbf{G}|^2}{2m} \leq E_{cut}$$

Kohn-Sham equations (assuming "local" potential)

$$\left(-\frac{\hbar^2\nabla^2}{2m} + V_{eff}(\mathbf{r})\right)\Psi_{nk}(\mathbf{r}) = E_{nk}\Psi_{nk}(\mathbf{r})$$

$$V_{eff}(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{V}_{eff}(\mathbf{G})e^{i\mathbf{G}\cdot\mathbf{r}}$$

$$\tilde{V}_{eff}(\mathbf{G}) = \int d^3r\, V_{eff}(\mathbf{r})\, e^{-i\mathbf{G}\cdot\mathbf{r}}$$

Convenient representation provided that

$$\left|\tilde{V}_{eff}(\mathbf{G})\right| < \epsilon \quad \text{for} \quad |\mathbf{G}| \geq G_{\max}$$

➔Strong motivation for the development of pseudopotentials

How can we construct a pseudopotential?

Norm-conserving pseudopotentials

VOLUME 43, NUMBER 20 PHYSICAL REVIEW LETTERS 12 NOVEMBER 1979

Norm-Conserving Pseudopotentials

D. R. Hamann, M. Schlüter, and C. Chiang
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 1 August 1979)

A very simple procedure to extract pseudopotentials from *ab initio* atomic calculations is presented. The pseudopotentials yield exact eigenvalues and nodeless eigenfunctions which agree with atomic wave functions beyond a chosen radius r_c. Moreover, logarithmic derivatives of real and pseudo wave functions and their first energy derivatives agree for $r > r_c$ guaranteeing excellent transferability of the pseudopotentials.

J. Phys. C: Solid St. Phys., 13 (1980) L189–94. Printed in Great Britain

LETTER TO THE EDITOR

Non-singular atomic pseudopotentials for solid state applications

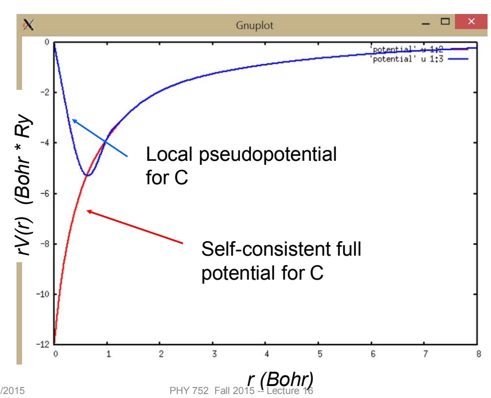
G P Kerker
Max-Planck-Institut für Festkörperforschung, 7000 Stuttgart 80, Heisenbergstrasse 1, West Germany

PHYSICAL REVIEW B VOLUME 43, NUMBER 3 15 JANUARY 1991-II

Efficient pseudopotentials for plane-wave calculations

N. Troullier and José Luís Martins
Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455
(Received 3 August 1990)

We present a simple procedure to generate first-principles norm-conserving pseudopotentials, which are designed to be smooth and therefore save computational resources when used with a plane-wave basis. We found that these pseudopotentials are extremely efficient for the cases where the plane-wave expansion has a slow convergence, in particular, for systems containing first-row elements, transition metals, and rare-earth elements. The wide applicability of the pseudopotentials are exemplified with plane-wave calculations for copper, zinc blende, diamond, α-quartz, rutile, and cerium.



Some details of pseudopotential construction from Troullier and Martins

Atomic Kohn-Sham equation for all-electron potential (atomic (Hartree) units

$$\left[\frac{-1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}+V^{AE}[\rho;r]\right]rR^{AE}_{nl}(r)=\varepsilon_{nl}rR^{AE}_{nl}(r) \ ,$$

Corresponding atomic Kohn-Sham equation for pseudoptential

$$\left[\frac{-1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}+V^{PP}[\rho;r]\right]rR^{PP}_{nl}(r)=\varepsilon_{nl}rR^{PP}_{nl}(r) \ ,$$

Conditions of *AE* and *PP* functions:

$$R_l^{\mathrm{PP}}(r)=R_l^{\mathrm{AE}}(r) \quad \text{for } r>r_{cl} \ ,$$

$$\int_0^{r_{cl}}|R_l^{\mathrm{PP}}(r)|^2r^2\,dr=\int_0^{r_{cl}}|R_l^{\mathrm{AE}}(r)|^2r^2\,dr \ .$$

$$\varepsilon_l^{\mathrm{PP}}=\varepsilon_l^{\mathrm{AE}} \ .$$

$$\frac{1}{R_l^{\mathrm{PP}}(r,\varepsilon)}\frac{dR_l^{\mathrm{PP}}(r,\varepsilon)}{dr}=\frac{1}{R_l^{\mathrm{AE}}(r,\varepsilon)}\frac{dR_l^{\mathrm{AE}}(r,\varepsilon)}{dr} \ .$$

Benefit of these conditions
➔Pseudo-wavefunction accurately represents correct functional form in valence region
➔Kohn-Sham equations correctly solved at energy of reference state and its neighborhood

$$-\frac{1}{2}\frac{\partial}{\partial\varepsilon}\frac{\partial}{\partial r}\ln R(r,\varepsilon)\bigg|_{\substack{\varepsilon=\varepsilon_l\\ r=r_{cl}}} =\frac{1}{r_{cl}^2R^2(r_{cl},\varepsilon_l)}\int_0^{r_{cl}}R^2(r,\varepsilon_l)r^2dr \ .$$

Troullier-Martins recipe

$$R_l^{\mathrm{PP}}(r)=\begin{cases} R_l^{\mathrm{AE}}(r) & \text{if } r \geq r_{cl} \\ r^l \exp[p(r)] & \text{if } r \leq r_{cl} \end{cases}, \tag{21}$$

$$p(r)=c_0+c_2r^2+c_4r^4+c_6r^6+c_8r^8+c_{10}r^{10}+c_{12}r^{12} .$$

$$V_{\mathrm{scr},l}(r)=\begin{cases} V_{\mathrm{AE}}(r) & \text{if } r \geq r_{cl} \\ \varepsilon_l+\dfrac{l+1}{r}\dfrac{p'(r)}{2}+\dfrac{p''(r)+[p'(r)]^2}{2} & \text{if } r \leq r_{cl} \end{cases}. \tag{23}$$

Conditions to determine coefficients c_n

$$2c_0+\ln\left[\int_0^{r_{cl}} r^{2(l+1)}\exp[2p(r)-2c_0]dr\right] =\ln\left[\int_0^{r_{cl}} |R_l^{\mathrm{AE}}(r)|^2 r^2 dr\right] .$$

Conditions on coeffients, continued:

$$p(r_{cl})=\ln\left[\frac{P(r_{cl})}{r_{cl}^{l+1}}\right],$$

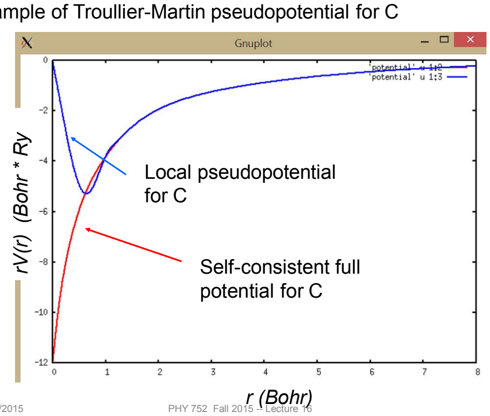
$$p'(r_{cl})=\frac{P'(r_{cl})}{P(r_{cl})}-\frac{l+1}{r_{cl}},$$

$$p''(r_{cl})=2V_{\mathrm{AE}}(r_{cl})-2\varepsilon_l -\frac{2(l+1)}{r_{cl}}p'(r_{cl})-[p'(r_{cl})]^2 ,$$

$$p'''(r_{cl})=2V'_{\mathrm{AE}}(r_{cl})+\frac{2(l+1)}{r_{cl}^2}p'(r_{cl}) -\frac{2(l+1)}{r_{cl}}p''(r_{cl})-2p'(r_{cl})p''(r_{cl}) ,$$

$$p''''(r_{cl})=2V''_{\mathrm{AE}}(r_{cl})-\frac{4(l+1)}{r_{cl}^3}p'(r_{cl}) +\frac{4(l+1)}{r_{cl}^2}p''(r_{cl})-\frac{2(l+1)}{r_{cl}}p'''(r_{cl}) -2[p''(r_{cl})]^2-2p'(r_{cl})p'''(r_{cl}) ,$$

Example of Troullier-Martin pseudopotential for C



according to

Pseudopotential form in terms of polynomial *p(r):*

$$V^{PS}(r) = E + \frac{\hbar^2}{2m}\left(\frac{d^2p}{dr^2} + \left(\frac{dp}{dr}\right)^2 + + \frac{2(L_v+1)}{r}\frac{dp}{dr}\right). \tag{9}$$

By construction, this function and its first two derivatives are equal to $v_{\text{eff}}(r)$ for $r \geq r_c$.

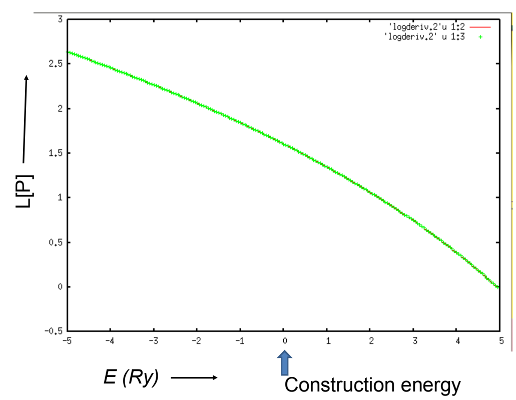
At this point, we can construct a smooth pseudo-Hamiltonian analogous the all-electron Hamiltonian (2) of the form

$$\tilde{H}(r) \equiv -\frac{\hbar^2}{2m}\nabla^2 + V^{PS}(r). \tag{10}$$

Properties of pseudopotential and corresponding pseudo-wavefunctions

➔Correct logarithmic derivatives at energy *E* and at nearby energies

$$L\left[P_{nl}(r_c)\right] \equiv \frac{d}{dr}\ln\left(\left[P_{nl}(r)\right]\right)\Big|_{r_c} = \frac{1}{P_{nl}(r_c)}\frac{dP_{nl}(r)}{dr}\Big|_{r_c}$$



Useful relationship in Rydberg units

$$\left(-\left(\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2}\right) + V_{eff}(r)\right)P_{n_il_i}(r) = E_{n_il_i}P_{n_il_i}(r)$$

Formally take energy derivative:

$$\left(-\left(\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2}\right) + V_{eff}(r) - E_{n_il_i}\right)\frac{dP_{n_il_i}(r)}{dE_{n_il_i}} = P_{n_il_i}(r)$$

$$-\left(P_{n_il_i}(r)\right)^2 \frac{d}{dE_{n_il_i}} L[P_{n_il_i}(r)]\Big|_{r_c} = \int_0^{r_c} dr\left(P_{n_il_i}(r)\right)^2$$

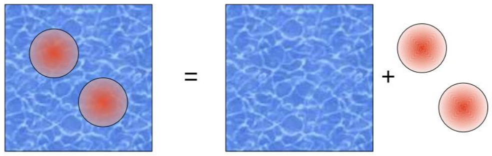
The construction ensures that

➔PS and AE have same log derivatives near E

➔What about other partial waves? (Non-local contributions to pseudopotential)

PAW representation of Kohn-Sham orbitals

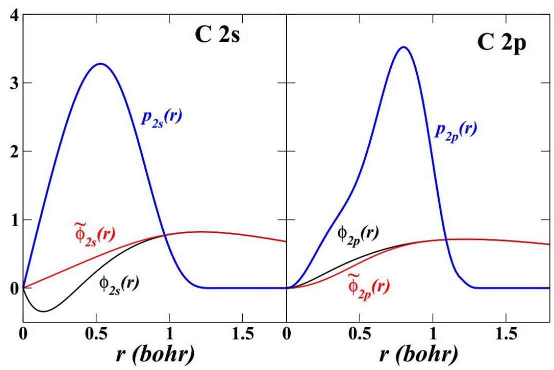
$$\Psi_v(\mathbf{r}) = \widetilde{\Psi}_v(\mathbf{r}) + \sum_{ai} \left(\phi_i^a(\mathbf{r}-\mathbf{R}^a) - \widetilde{\phi}_i^a(\mathbf{r}-\mathbf{R}^a) \right) \langle p_i^a | \widetilde{\psi}_v \rangle,$$



Evaluation of the energy of the system

$$E_{tot}^{\text{vale}} = \underbrace{\widetilde{E}_{tot}}_{\text{pseudo energy}} + \sum_a \underbrace{\left(E_{tot}^a - \widetilde{E}_{tot}^a \right)}_{\text{atom-centered corrections}} .$$

Example of atomic basis and projector functions



Clever secret of PAW method; partitioning of planewave and one center contributions

The product of two wavefunctions $P_{vw}(\mathbf{r}) \equiv \Psi_v^*(\mathbf{r})\Psi_w(\mathbf{r})$ can be well-approximated with the form

$$P_{vw}(\mathbf{r}) = \widetilde{P}_{vw}(\mathbf{r}) + \sum_a \left(P_{vw}^a(\mathbf{r}-\mathbf{R}^a) - \widetilde{P}_{vw}^a(\mathbf{r}-\mathbf{R}^a) \right), \tag{26}$$

where

$$\widetilde{P}_{vw}(\mathbf{r}) \equiv \widetilde{\Psi}_v^*(\mathbf{r})\widetilde{\Psi}_w(\mathbf{r}), \tag{27}$$

and

$$P_{vw}^a(\mathbf{r}) - \widetilde{P}_{vw}^a(\mathbf{r}) \equiv \sum_{ij} \langle \widetilde{\Psi}_v | p_i^a \rangle \langle p_j^a | \widetilde{\Psi}_w \rangle \left(\phi_i^{a*}(\mathbf{r})\phi_j^a(\mathbf{r}) - \widetilde{\phi}_i^{a*}(\mathbf{r})\widetilde{\phi}_j^a(\mathbf{r}) \right). \tag{28}$$

Equivalently, we can write:

$$P_{vw}(\mathbf{r}) = \widetilde{P}_{vw}(\mathbf{r}) + \widehat{P}_{vw}(\mathbf{r}) + \sum_a \left(P_{vw}^a(\mathbf{r}-\mathbf{R}^a) - \widetilde{P}_{vw}^a(\mathbf{r}-\mathbf{R}^a) - \widehat{P}_{vw}^a(\mathbf{r}-\mathbf{R}^a) \right), \tag{29}$$

where the "compensation charge"

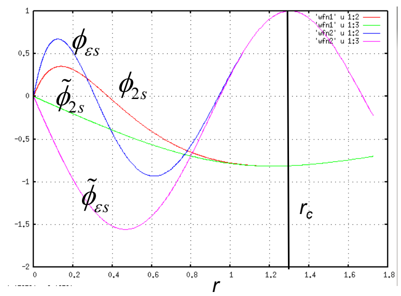
$$\widehat{P}_{vw}(\mathbf{r}) \equiv \sum_a \widehat{P}_{vw}^a(\mathbf{r}-\mathbf{R}^a) \tag{30}$$

is a smooth function localized within the atomic augmentation spheres such that:

$$\int d^3r' \, \frac{P_{vw}^a(\mathbf{r}') - \tilde{P}_{vw}^a(\mathbf{r}') - \hat{P}_{vw}^a(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = \begin{cases} V_{vw}^a(\mathbf{r}) & \text{for} \quad |\mathbf{r}-\mathbf{R}^a| \le r_c^a \\ 0 & \text{otherwise} \end{cases} . \tag{31}$$

Construction of atom centered basis and projector functions:

$$\left(\mathcal{H}^{\mathrm{KS}}(\mathbf{r})-\varepsilon_i^a\right)\Phi_i^a(\mathbf{r})=0$$



Construction of atom centered basis and projector functions – continued (scheme developed by David Vanderbilt for ultra-soft pseudopotentials; for each *l* channel at at time):

$$\text{Let}\quad \tilde{\phi}_i(r)=\begin{cases} r^{l_i+1}\sum_{m=1}^{4}C_m r^{2m} & r<r_c \\ \phi_i(r) & r>r_c \end{cases}$$

Construct auxiliary function:

$$\chi_i(r)=\left(\varepsilon_i-\tilde{\mathcal{H}}^{\mathrm{KS}}\right)\tilde{\phi}_i(r)$$

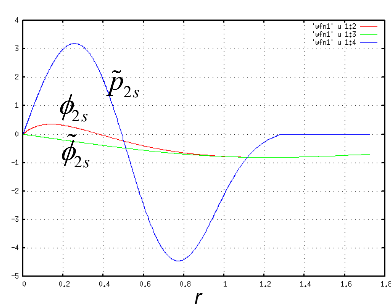
Calculate overlap matrix: $B_{ij}\equiv\langle\chi_i|\chi_j\rangle$

Form projector function: $p_i(r)=\sum_j \chi_j(r)\left(\mathbf{B}^{-1}\right)_{ji}$

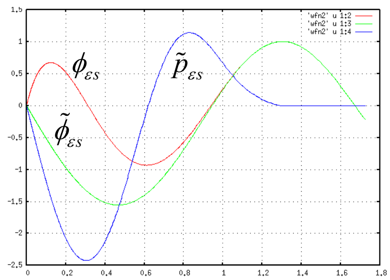
This construction ensures that

$$\left\langle\tilde{P}_j^a(\mathbf{r})\middle|\tilde{\Phi}_i^a\right\rangle=\delta_{ij}$$

Example for C



Example for C -- continued



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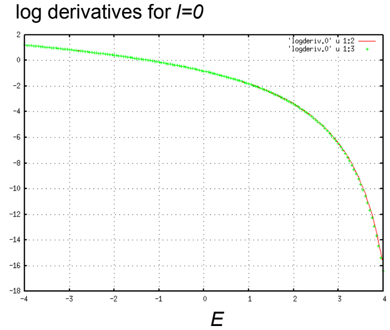
Example for C -- continued
log derivatives for *l=0*



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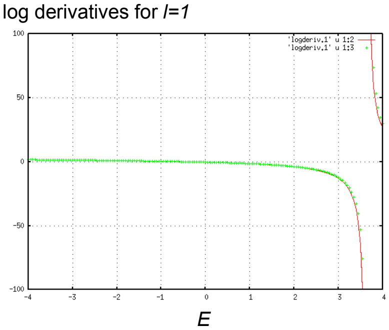
Example for C -- continued
log derivatives for *l=1*



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Example for C -- continued

log derivatives for *l=2*