PHY 752 Solid State Physics
11-11:50 AM MWF Olin 107

Plan for Lecture 16:
Reading: Chapter 10 in MPM
Numerical Realizations of Density functional theory

1. Running graphatom code for spherical atoms
2. Introduction to pseudopotentials
3. Projector Augmented Wave (PAW) approximation

	Lecture date	MPM Reading	Topic	Assign.	Due date
1	Mon: 01/12/2015	Chap. 1 & 2	Crystal structures	#1	01/23/2015
2	Wed: 01/14/2015	Chap. 1 & 2	Some group theory	#2	01/23/2015
	Fri: 01/16/2015	No class	NAWH out of town		
	Mon: 01/19/2015	No class	MLK Holiday		
3	Wed: 01/21/2015	Chap. 1 & 2	Some group theory	#3	01/23/2015
4	Fri: 01/23/2015	Chap. 1 & 2	Some more group theory	#4	01/26/2015
5	Mon: 01/26/2015	Chap. 7.3	Some more group theory	#5	01/28/2015
6	Wed: 01/28/2015	Chap. 6	Electronic structure; Free electron gas	#6	01/30/2015
7	Fri: 01/30/2015	Chap. 7	Electronic structure; Model potentials	#7	02/02/2015
8	Mon: 02/02/2015	Chap. 8	Electronic structure; LCAO	#8	02/04/2015
9	Wed: 02/04/2015	Chap. 8	Electronic structure; LCAO and tight binding	#9	02/06/2015
10	Fri: 02/06/2015	Chap. 8	Band structure examples	#10	02/09/2015
11	Mon: 02/09/2015	Chap. 9	Electron-electron interactions	#11	02/11/2015
12	Wed: 02/11/2015	Chap. 9	Electron-electron interactions	#12	02/13/2015
13	Fri: 02/13/2015	Chap. 9	Electron-electron interactions	#13	02/16/2015
14	Mon: 02/16/2015	Chap. 10	Electronic structure calculation methods	#14	02/18/2015
15	Wed: 02/18/2015	Chap. 10	Electronic structure calculation methods	#15	02/20/2015
16	Fri: 02/20/2015	Chap. 10	Electronic structure calculation methods	#16	02/23/2015

Note: Take-home exam scheduled for the week of March 2nd.

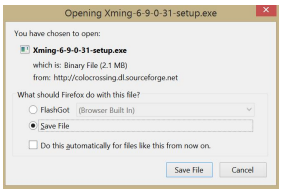
Some comments on using the cluster

Necessary software on your laptop:

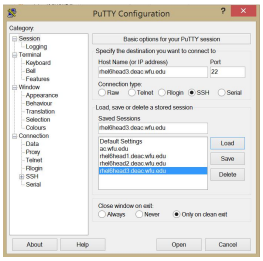
1. A terminal emulator. For windows this means Virtual Box or Putty

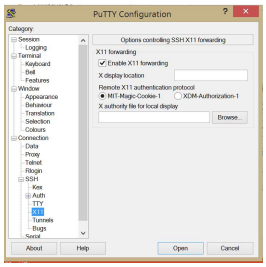
2. If you use Putty, you will also need a graphics emulator such as Xming

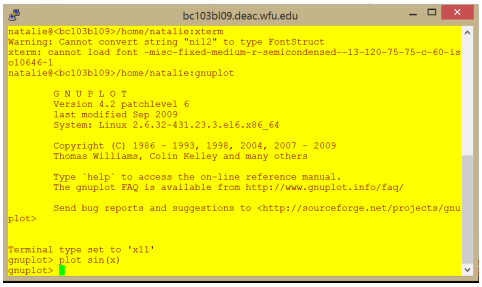
http://sourceforge.net/projects/xming/

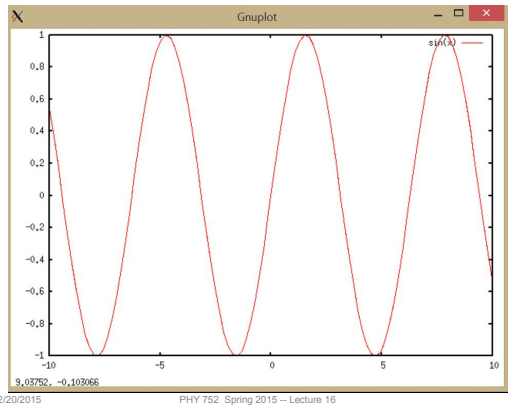


When you run Putty to access the cluster, Xming should be running in background.









If this is the first time using the cluster – you may which to:

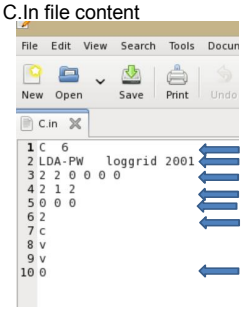
- In your home directory (/home/login)
  cp /home/natalie/EL6/Coursematerials/s15phy752/setups/.tcshrc .
- source .tcshrc

Course datafiles
/wfurc1/classes/phy752/login

To do the graphatom homework, do the following:

- cd /wfurc1/classes/phy752/login
- /wfurc1/classes/phy752/natalie: mkdir C
- /wfurc1/classes/phy752/natalie: cd C
- /wfurc1/classes/phy752/natalie/C: gedit C.in
- /wfurc1/classes/phy752/natalie/C: \
  ~natalie/EL6/Coursematerials/s15phy752/pgms/rungraphatom <C.in>&out&

C.In file content



Atomic symbol & number
Exchange-correl. Type & grid info
Maximum *n* for *l=1,2,3,4…..*
n l occ corrected configuration
End configuration changes
Flag for frozencore setting

End program


```
natalie@<bc103bl09>/wfurc1/classes/phy752/natalie/Graphatom-C:~natalie/EL6/Cou
ematerials/s15phy752/pgms/rungraphatom <C.in>&out&
[1] 28449
natalie@<bc103bl09>/wfurc1/classes/phy752/natalie/Graphatom-C:lft
total 0
-rw-rw-r--  1 natalie natalie  31383 Feb 19 17:48 out
-rw-rw-r--  1 natalie natalie  80066 Feb 19 17:48 densitySC.GA
drwxrwxr-x  2 natalie natalie    512 Feb 19 17:48 ./
-rw-rw-r--  1 natalie natalie   1188 Feb 19 17:48 C.GA
-rw-rw-r--  1 natalie natalie 122061 Feb 19 17:48 wfnSC1
-rw-rw-r--  1 natalie natalie 122061 Feb 19 17:48 potSC1
-rw-rw-r--  1 natalie natalie  40850 Feb 19 17:48 potential.GA
-rw-rw-r--  1 natalie natalie  40850 Feb 19 17:48 density.GA
-rw-rw-r--  1 natalie natalie 122061 Feb 19 17:48 wfnAE0
-rw-rw-r--  1 natalie natalie 122061 Feb 19 17:48 potAE0
-rw-rw-r--  1 natalie natalie     51 Feb 19 17:48 dummy
-rw-rw-r--  1 natalie natalie     62 Feb 19 17:46 C.in
drwxr-xr-x. 4 natalie classes    512 Feb 19 17:44 ../
[1]  + Done                       ~natalie/EL6/Coursematerials/s15phy752/pg
/rungraphatom < C.in >& out
```



```
 Completed calculations for C
 Perdew-Wang LDA -- PRB 45, 13244 (1992)
  Radial integration grid is logarithmic
r0 =   9.4549737E-04 h =   5.6729242E-03   n =      2001 rmax =   8.0000000E
 Non-relativistic calculation
   AEatom converged in          21  iterations
     for nz =   0.00
     delta  =   7.163706946927433E-017

 Orbital energies
 n  l     occupancy              energy
 1  0      2.0000000E+00 -1.9895104E+01
 2  0      2.0000000E+00 -1.0016119E+00
 2  1      2.0000000E+00 -3.9828763E-01

  Total energy
     Total                  :    -74.8487453198796

   FCatom converged in           1  iterations
     for nz =   0.00
     delta  =   1.052568767265659E-017

Orbital energies
n  l     occupancy              energy
2  0      2.0000000E+00 -1.0016119E+00
2  1      2.0000000E+00 -3.9828763E-01

 Total energy
    Total                   :    -74.8487453191085
    Valence                 :    -17.0691384266577
```

Some output --
densitySC.GA:

# r	core den	vale den	total den
0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
5.3789E-06	4.3545E-08	2.2601E-09	4.5806E-08
1.0788E-05	1.7516E-07	9.0912E-09	1.8425E-07
1.6229E-05	3.9634E-07	2.0571E-08	4.1691E-07
2.1700E-05	7.0858E-07	3.6776E-08	7.4535E-07
2.7202E-05	1.1134E-06	5.7787E-08	1.1712E-06
3.2736E-05	1.6124E-06	8.3684E-08	1.6960E-06
3.8301E-05	2.2070E-06	1.1455E-07	2.3216E-06
4.3898E-05	2.8990E-06	1.5046E-07	3.0494E-06
4.9527E-05	3.6898E-06	1.9151E-07	3.8813E-06
5.5187E-05	4.5811E-06	2.3777E-07	4.8189E-06

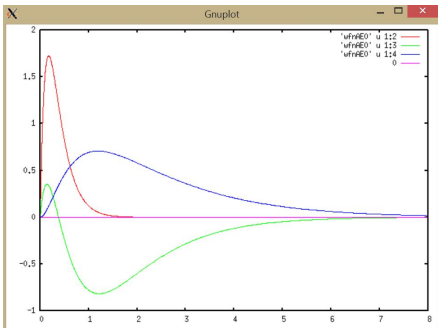
wfnAE0:

r	*1s*	*2s*	*2p*
0.0000000E+00	0.0000000E+00	0.0000000E+00	0.0000000E+00
5.3789209E-06	1.4755592E-04	3.3616047E-05	1.8374828E-10
1.0788443E-05	2.9594168E-04	6.7421149E-05	7.3916846E-10
1.6228740E-05	4.4516190E-04	1.0141636E-04	1.6725858E-09
2.1699987E-05	5.9522122E-04	1.3560273E-04	2.9904092E-09
2.7202360E-05	7.4612429E-04	1.6998132E-04	4.6991324E-09
3.2736036E-05	8.9787581E-04	2.0455320E-04	6.8053347E-09
3.8301194E-05	1.0504805E-03	2.3931945E-04	9.3156826E-09

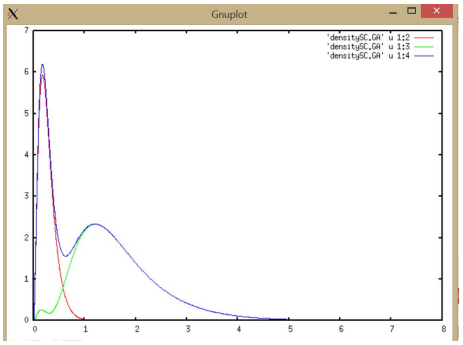
Plotting results with gnuplot:

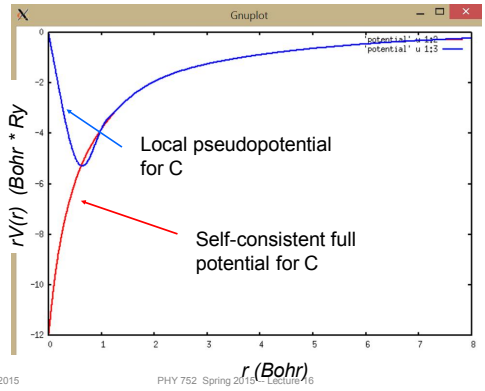
```
natalie@<bc103b109>/wfurc1/classes/phy752/natalie/Graphatom-C:gnuplot

        G N U P L O T
        Version 4.2 patchlevel 6
        last modified Sep 2009
        System: Linux 2.6.32-431.23.3.el6.x86_64

        Copyright (C) 1986 - 1993, 1998, 2004, 2007 - 2009
        Thomas Williams, Colin Kelley and many others

        Type `help` to access the on-line reference manual.
        The gnuplot FAQ is available from http://www.gnuplot.info/faq/

        Send bug reports and suggestions to <http://sourceforge.net/projects/gnu
plot>

Terminal type set to 'x11'
gnuplot> plot 'wfnAE0' u 1:2 w l, 'wfnAE0' u 1:3 w l, 'wfnAE0' u 1:4 w l
```


plot [0:8] 'wfnAE0' u 1:2 w l, 'wfnAE0' u 1:3 w l, 'wfnAE0' u 1:4 w l,0



plot [0:8] 'densitySC.GA' u 1:2 w l, 'densitySC.GA' u 1:3 w l, 'densitySC.GA' u 1:4 w l





Motivation/justification for pseudopotential formalism

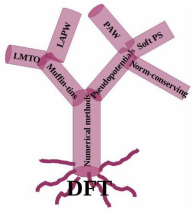
PHYSICAL REVIEW VOLUME 116, NUMBER 2 OCTOBER 15, 1959

New Method for Calculating Wave Functions in Crystals and Molecules*

JAMES C. PHILLIPS† AND LEONARD KLEINMAN‡
Department of Physics, University of California, Berkeley, California
(Received January 5, 1959; revised manuscript received June 1, 1959)

For metals and semiconductors the calculation of crystal wave functions is simplest in a plane wave representation. However, in order to obtain rapid convergence it is necessary that the valence electron wave functions be made orthogonal to the core wave functions. Herring satisfied this requirement by choosing as basis functions "orthogonalized plane waves." It is here shown that advantage can be taken of crystal symmetry to construct wave functions ϕ_k, which are best described as the smooth part of symmetrized Bloch functions. The wave equation satisfied by ϕ_k contains an additional term of simple character which corresponds to the usual complicated orthogonalization terms and has a simple physical interpretation as an effective repulsive potential. Qualitative estimates of this potential in analytic form are presented. Several examples are worked out which display the cancellation between attractive and repulsive potentials in the core region which is responsible for rapid convergence of orthogonalized plane wave calculations for s states; the slower convergence of p states is also explained. The formalism developed here can also be regarded as a rigorous formulation of the "empirical potential" approach within the one-electron framework; the present results are compared with previous approaches. The method can be applied equally well to the calculation of wave functions in molecules.

Projector Augmented Wave method – quick summary



The PAW formalism was developed by P. Blöchl (*PRB* **50**, 17953–17979 (1994)), having similarities to the soft-pseudopotential formalism of D. Vanderbilt (*PRB* **41** 7892-7895 (1990)). One distinguishing feature of PAW, is the transformation between all-electron valence wavefunctions $\Psi_v(\mathbf{r})$ and $\widetilde{\Psi}_v(\mathbf{r})$:

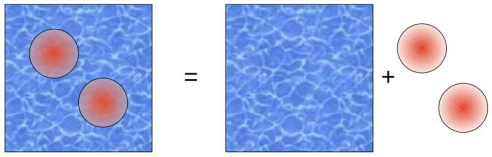
$$\Psi_v(\mathbf{r}) = \widetilde{\Psi}_v(\mathbf{r}) + \sum_{ai} \left(\phi_i^a(\mathbf{r}-\mathbf{R}^a) - \widetilde{\phi}_i^a(\mathbf{r}-\mathbf{R}^a)\right)\langle p_i^a|\widetilde{\Psi}_v\rangle, \quad (23)$$

where ϕ_i^a, $\widetilde{\phi}_i^a$, and p_i^a are atom-centered all-electron basis, pseudo-electron basis, and projector functions, respectively.

Computational work is performed on pseudofunctions $\widetilde{\Psi}_v(\mathbf{r})$ after which all-electron functions $\Psi_v(\mathbf{r})$ can be retreived from PAW transformation.

PAW representation of Kohn-Sham orbitals

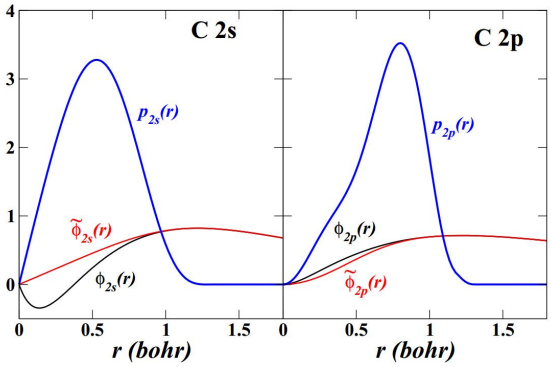
$$\Psi_v(\mathbf{r}) = \widetilde{\Psi}_v(\mathbf{r}) + \sum_{ai}\left(\phi_i^a(\mathbf{r}-\mathbf{R}^a) - \widetilde{\phi}_i^a(\mathbf{r}-\mathbf{R}^a)\right)\langle p_i^a|\widetilde{\psi}_v\rangle,$$



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

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

where

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

and

$$P^a_{vw}(\mathbf{r}) - \widetilde{P}^a_{vw}(\mathbf{r}) \equiv \sum_{ij} \langle \widetilde{\Psi}_v | p^a_i \rangle \langle p^a_j | \widetilde{\Psi}_w \rangle \left(\phi^{a*}_i(\mathbf{r})\phi^a_j(\mathbf{r}) - \widetilde{\phi}^{a*}_i(\mathbf{r})\widetilde{\phi}^a_j(\mathbf{r}) \right). \tag{28}$$

Equivalently, we can write:

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

where the "compensation charge"

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

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

$$\int d^3r' \frac{P^a_{vw}(\mathbf{r}') - \tilde{P}^a_{vw}(\mathbf{r}') - \hat{P}^a_{vw}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = \begin{cases} V^a_{vw}(\mathbf{r}) & \text{for } |\mathbf{r}-\mathbf{R}^a| \le r^a_c \\ 0 & \text{otherwise} \end{cases}. \tag{31}$$