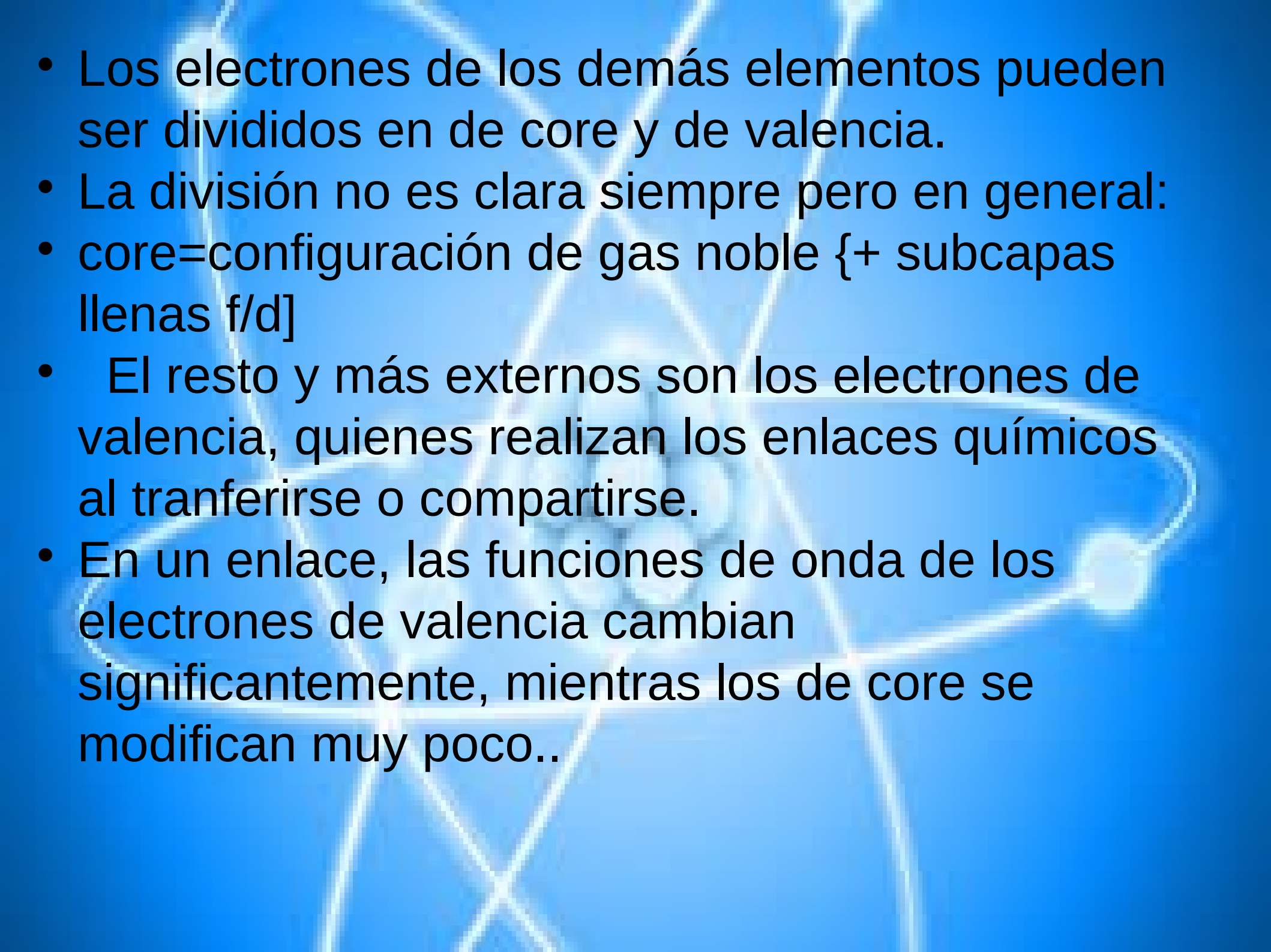


Uso de bases atómicas y pseudopotenciales en Química Cuántica.

JF Rivas Silva
IFUAP

La estructura electrónica de los átomos está especificada por los números cuánticos: n capas, l subcapas, m_l orbitales, m_s spin.

Los átomos de gases nobles tienen subcapas completas (inertes): He $1s^2$, Ne $[\text{He}]2s^22p^6$, Ar $[\text{Ne}]3s^23p^6$, .. Rn $[\text{Xe}]4f^{14}5d^{10}6s^26p^6$.

- 
- Los electrones de los demás elementos pueden ser divididos en de core y de valencia.
 - La división no es clara siempre pero en general:
 - core=configuración de gas noble {+ subcapas llenas f/d]
 - El resto y más externos son los electrones de valencia, quienes realizan los enlaces químicos al transferirse o compartirse.
 - En un enlace, las funciones de onda de los electrones de valencia cambian significativamente, mientras los de core se modifican muy poco..

- La aproximación de los pseudopotenciales radica en considerar a los electrones de valencia sujetos a la interacción debida a los núcleos y a los electrones de core, siendo ésta representada por un potencial efectivo.
-
- Hay que hallar la solución de la ecuación de las QC para el sistema de los electrones en el átomo:
- Según el nivel de teoría: Schroedinger o Dirac.
- Según el principio de mínima energía a utilizar: HF o DFT
-
-
-

- Se acepta la aproximación de simetría esférica efectiva: $\psi_{lms}(r) = R_{nl}(r) Y_{lm}(\theta, \varphi) \sigma_s$.
- *Las ecuaciones se resuelven para todos los electrones (all-electron).*
- *Debe considerarse que:*
- *Al ser el hamiltoniano un operador hermítico, sus eigenvalores son reales.*
- *Las eigenfunciones son ortonormales.*
- *(nótese que esto impone una especie de interacción efectiva entre electrones, en particular del core a los de valencia!).*

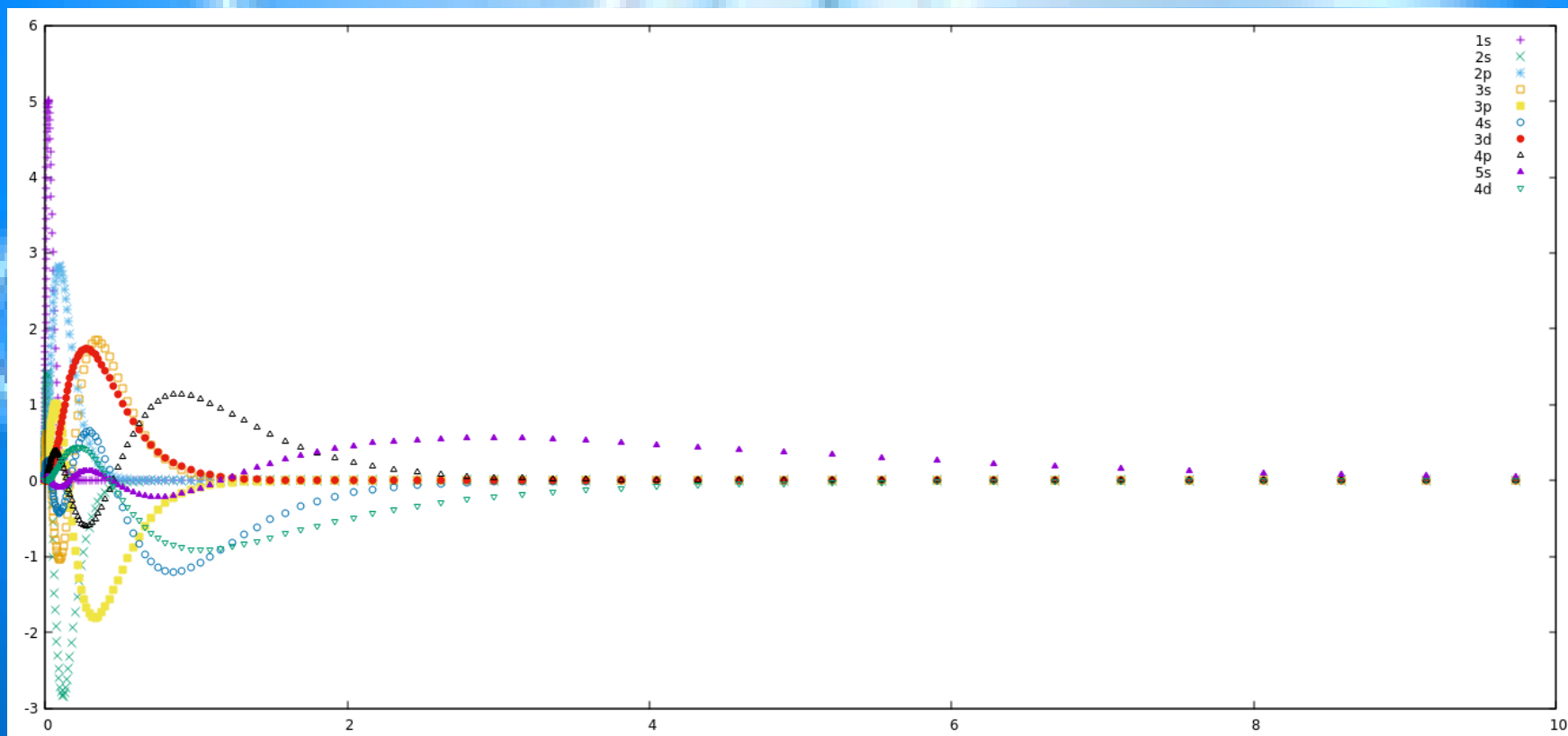
-
-
-

- Cálculos atómicos: Ej. Programa de C.F. Fischer
- (1977)

<https://niste.nist.gov/cgi-bin/MCHF/download.pl?d=HF>

- Ejemplo:

47Ag=1s22s22p63s23p64s23d104p65s14d10



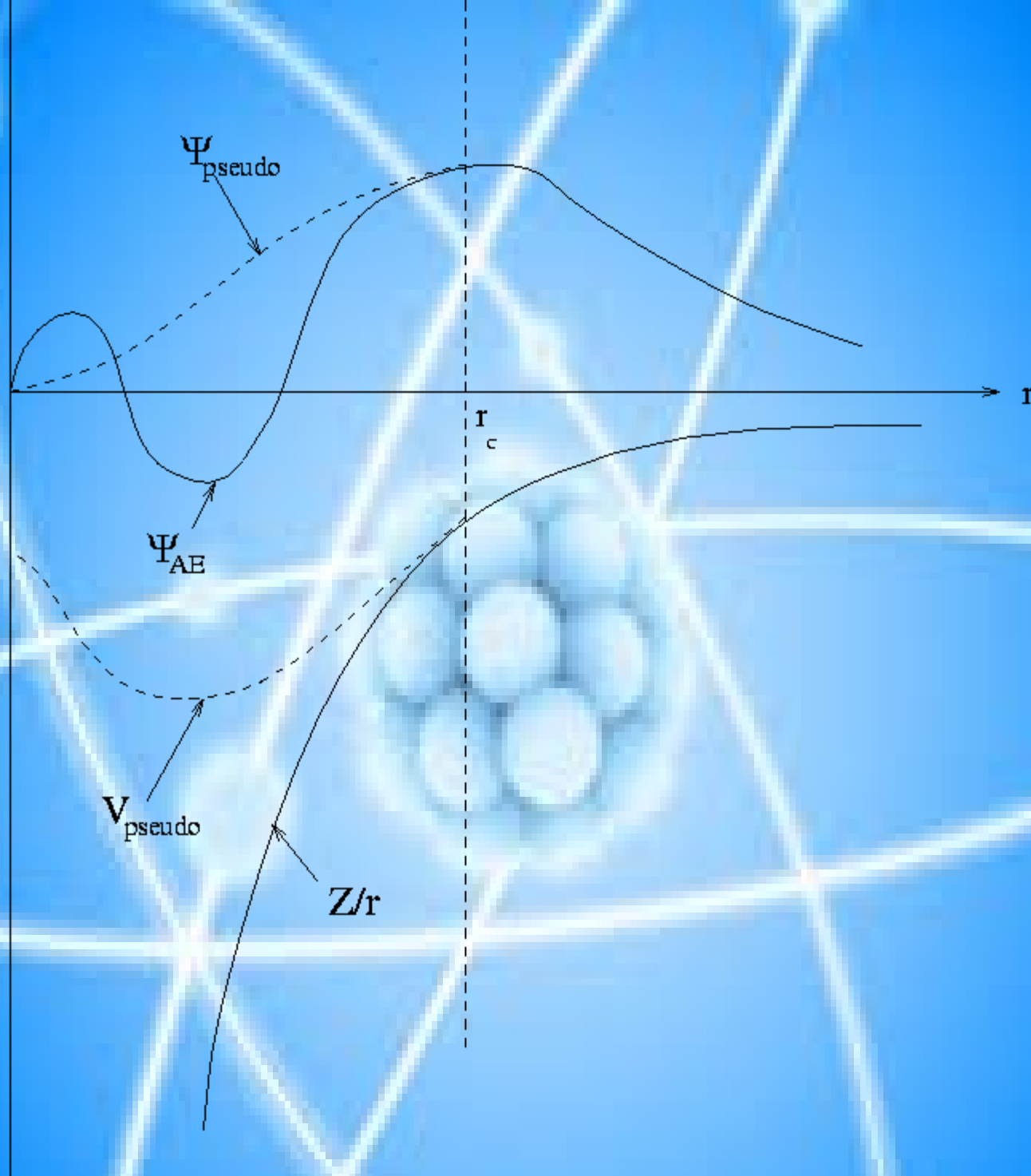
Ideas generales de la aproximación de los Pseudopotenciales:

1. Remover los electrones de core (disminuir esos grados de libertad)
2. Sustituir su efecto sobre los de valencia a través de un potencial efectivo que es agregado al del núcleo.
3. Esto dá sistemas electrónicos de menor tamaño y entonces más manejables.
4. Se pierde exactitud. El error es de segundo orden en $\Delta\rho = \rho \text{ true} - \rho \text{ frozen-core}$.

Generando los Pseudopotenciales:

1. Elegir una distancia desde el núcleo atómico, llamada radio de corte r_c , aprox. intermedia al radio atómico.

- * Si es muy pequeña: ps muy duro
- * Muy grande, no muy transferible
- * Distinto para cada l
- * Mayor que el último nodo de la función radial
- * Recomendación: poco menor al último pico



2. Las funciones electrónicas de valencia son representadas por funciones que a partir del radio de corte r_c hacia afuera son idénticas a ellas, pero no hacia adentro. Estas nuevas funciones son llamadas pseudofunciones.. Nótese que éstas no oscilan allí dentro !

3. Estas funciones PSF resuelven la ecuación central a la que se le ha agregado el pseudopotencial, obteniéndose los e_v exactos. Nótese que el potencial original de Coulomb ha sido sustituido por el PS.

4. La forma del PS permite la “suavidad” de las PSF.

5. Primeramente SE DEBE resolver la ecuación central para obtener las funciones de onda y eigenvalores all electron, FAE y EAE.

6. Haciendo la elección de electrones de core y de valencia, se encuentra el potencial que sienten los electrones de valencia, invirtiendo la ecuación:

$$V_l^{scf}(r) = \epsilon_l - \frac{l(l+1)}{2r^2} + \frac{1}{2r\psi_l(r)} \frac{d^2[r\psi_l(r)]}{dr^2}$$

7. Se le quitan las contribuciones Hartree y XC:

$$V_l^{PS}(r) = V_l^{scf}(r) - V_H[\rho^{val}(r)] - V_{XC}[\rho^{val}(r)]$$

8. Condiciones adicionales que se deben cumplir:

* EAE = EPS

** Ecuaciones logarímicamente de continuidad en rc.

*** Conservación de norma:

$$\int_0^{r_c} r^2 \psi_{nl}^{*AE}(\mathbf{r}) \psi_{nl}^{AE}(\mathbf{r}) dr = \int_0^{r_c} \psi_l^{*PS}(\mathbf{r}) \psi_l^{PS}(\mathbf{r}) dr$$

**** Algunas veces ésta no se exige precisamente por conveniencia.

Pseudopotenciales desarrollados en la literatura:

Philipps, Kleinman (1958)

$$\hat{F} | \psi_v \rangle = \epsilon_v | \psi_v \rangle$$

$$\hat{F} | \psi_c \rangle = \epsilon_c | \psi_c \rangle, \quad \langle \psi_c | \psi_v \rangle = 0, \quad \langle \psi_c | \psi_{c'} \rangle = \delta_{cc'}$$

$$| \tilde{\psi}_v \rangle = a_v | \psi_v \rangle + \sum_c a_c | \psi_c \rangle$$

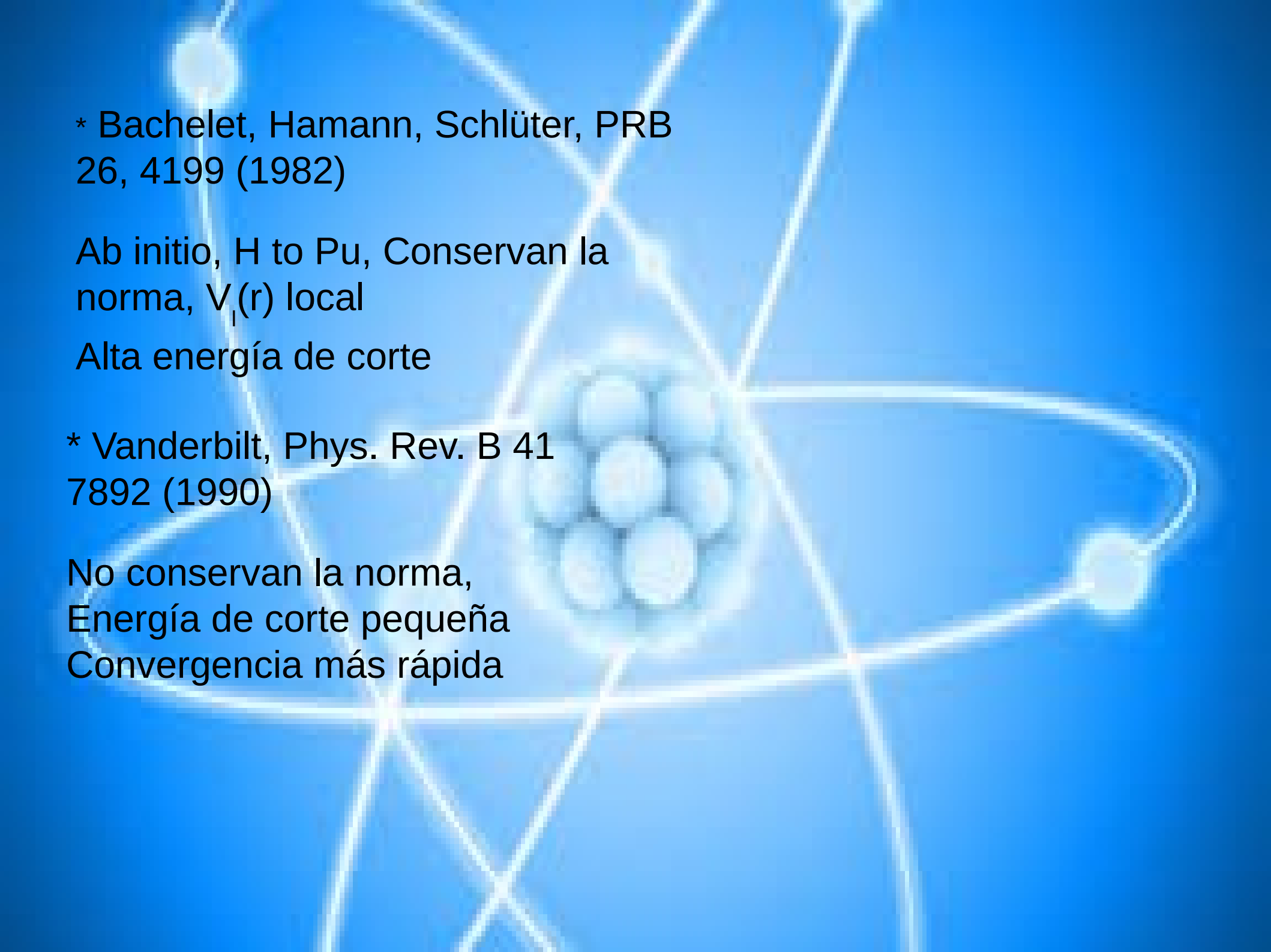
$$| \tilde{\psi}_v \rangle = a_v | \psi_v \rangle + \sum_c | \psi_c \rangle \langle \psi_c | \tilde{\psi}_v \rangle$$

(pseudoorbital)

$$\hat{F} | \tilde{\psi}_v \rangle - \sum_c \epsilon_c | \psi_c \rangle \langle \psi_c | \tilde{\psi}_v \rangle = \epsilon_v | \tilde{\psi}_v \rangle - \epsilon_v \sum_c | \psi_c \rangle \langle \psi_c | \tilde{\psi}_v \rangle$$

$$\left\{ \hat{F} + \sum_c (\epsilon_v - \epsilon_c) | \psi_c \rangle \langle \psi_c | \right\} | \tilde{\psi}_v \rangle = \epsilon_v | \tilde{\psi}_v \rangle$$

$$\hat{F}^{PK} | \tilde{\psi}_v \rangle = \epsilon_v | \tilde{\psi}_v \rangle$$



* Bachelet, Hamann, Schlüter, PRB
26, 4199 (1982)

Ab initio, H to Pu, Conservan la
norma, $V_l(r)$ local

Alta energía de corte

* Vanderbilt, Phys. Rev. B 41
7892 (1990)

No conservan la norma,
Energía de corte pequeña
Convergencia más rápida

Refinamientos:

* Kleinman-Bylander Transformation (PRL 48, 1425, 1982) (trabaja en G)

Pasar un potencial semilocal a una forma separable:

$$V_{ion} = \sum_{lm} |Y_{lm}\rangle V_l \langle Y_{lm}| \quad (3.37)$$

• Nonlocal: $V(r,r')$ [nonlocal in r & Ω]

Semilocal $V_l(r,r') = V_l(r)\delta(r-r')$

Local $V(r,r') = V_{loc}(r)\delta(r-r')\delta(\Omega,\Omega')$

• $V_l(r,r') = F_l^*(r)f_l(F_l(r'))$ [más rápida]

• Corrección no lineal: Louie, Froyen & Cohen, Phys. Rev. B 26 1738 (1982)]

Método de Projector augmented wave (PAWS)

Blöchl, P.E. (1994). "Projector augmented-wave method". Physical Review B. 50 (24): 17953–17978

$$|\psi_{nl}\rangle = T^- |\tilde{\psi}_{nl}\rangle$$

izq. función all electron, der. Pseudof.

$$T^- = 1 + \sum_a \sum_i (|\phi_{ai}\rangle - |\tilde{\phi}_{ai}\rangle)$$

$$\psi_n(\mathbf{r}) = \tilde{\psi}_n(\mathbf{r}) + \sum_a \sum_i (\phi_i^a(\mathbf{r}) - \tilde{\phi}_i^a(\mathbf{r})) \langle \tilde{p}_i^a | \tilde{\psi}_n \rangle,$$

PAWS para VASP:
PAW_PBE Ag_pv 09Dec2005
17.00000000000000

parameters from PSCTR are:

VRHFIN = Ag : s1 d10

LEXCH = PE

EATOM = 3061.0398 eV, 224.9801 Ry

TITEL = PAW_PBE Ag_pv 09Dec2005

LULTRA = F use ultrasoft PP ?

IUNSCR = 1 unscreen: 0-lin 1-nonlin 2-no

RPACOR = 2.000 partial core radius

POMASS = 107.868; ZVAL = 17.000 mass and valenz

RCORE = 2.200 outmost cutoff radius

RWIGS = 2.300; RWIGS = 1.217 wigner-seitz radius (au A)

ENMAX = 297.865; ENMIN = 223.399 eV

ICORE = 3 local potential

LCOR = T correct aug charges

LPAW = T paw PP

EAUG = 532.843

DEXC = 0.000

RMAX = 2.253 core radius for proj-oper

RAUG = 1.300 factor for augmentation sphere

RDEP = 2.266 radius for radial grids

RDEPT = 1.838 core radius for aug-charge

ATOMPAW

INFO

DATASETS

CONTRIBUTERS

CONTACT INFO

NAWH Web

PHYSICS Web

WFU Web

ATOMPAW

General information:

This code, originally written by N. A. W. Holzwarth, A. R. Tackett, and G. E. Matthews, is described in the publication *A Projector Augmented Wave (PAW) code for electronic structure calculations, Part I: atompaw for generating atom-centered functions* [Computer Physics Communications 135 329-347 \(2001\)](#) -- ([local copy](#)) -- With the help of several collaborators at Wake Forest University as well as several international collaborators, the code has been continually updated and adapted for use with various electronic structure codes including [abinit](#), [quantum-espresso](#), [socorro](#), and [pwpaw](#).

Feedback

We strongly encourage extensive testing of the datasets before using them on your research projects. Feedback on the code and on the atomic datasets is appreciated. Contact: natalie@wfu.edu Additional information on PAW datasets is available on the [abinit](#) website.

Thanks to Sina Zolghadr (with help from Eric Chapman) for the webpage design.

A Projector Augmented Wave (PAW) code for electronic structure calculations, Part I: *atompaw* for generating atom-centered functions

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^a *Department of Physics, Wake Forest University, Winston-Salem, NC 27109, USA*

^b *Department of Physics and Astronomy, Vanderbilt University, Nashville, TN 37235, USA*

Received 21 July 2000; accepted 26 October 2000

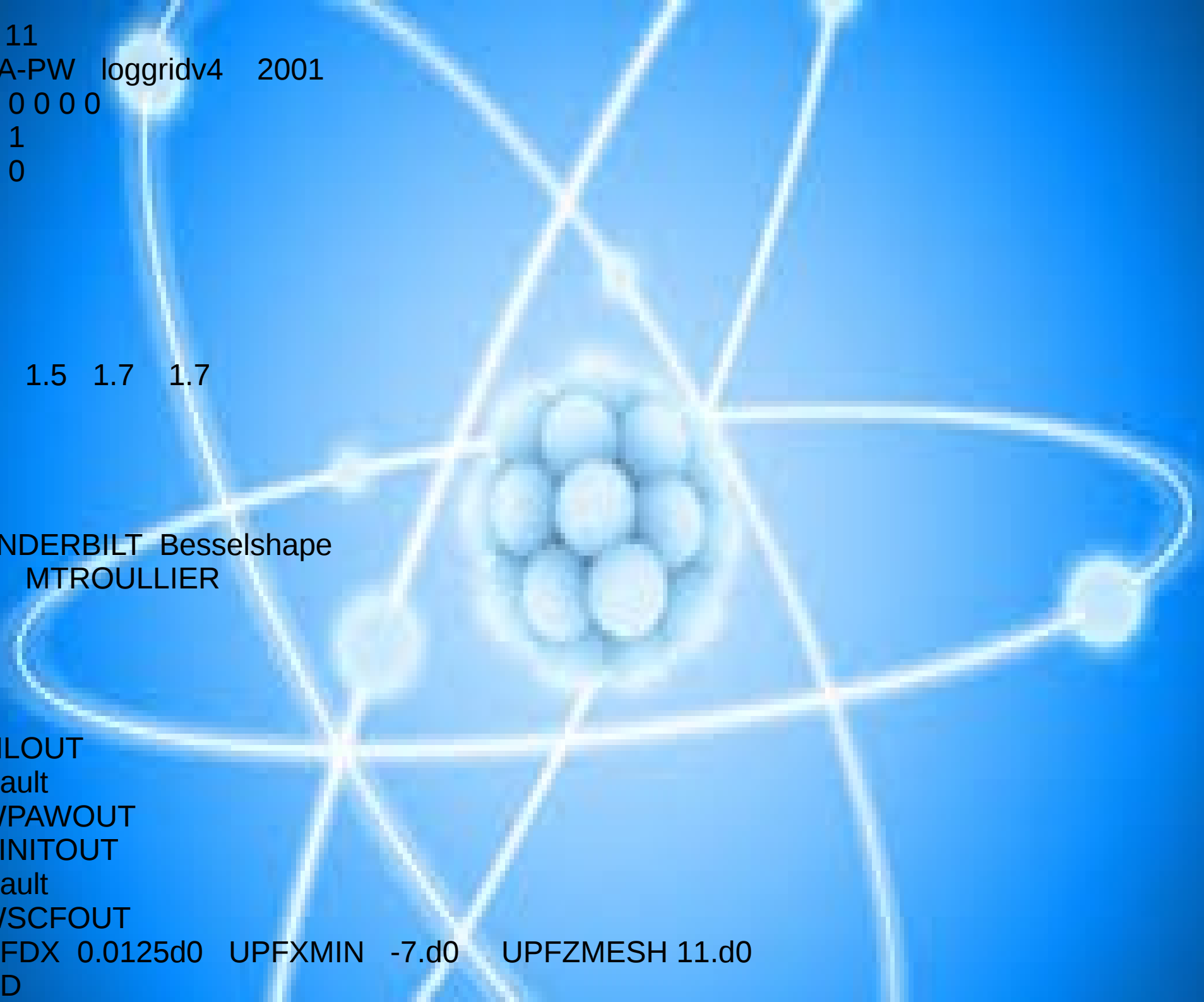
Abstract

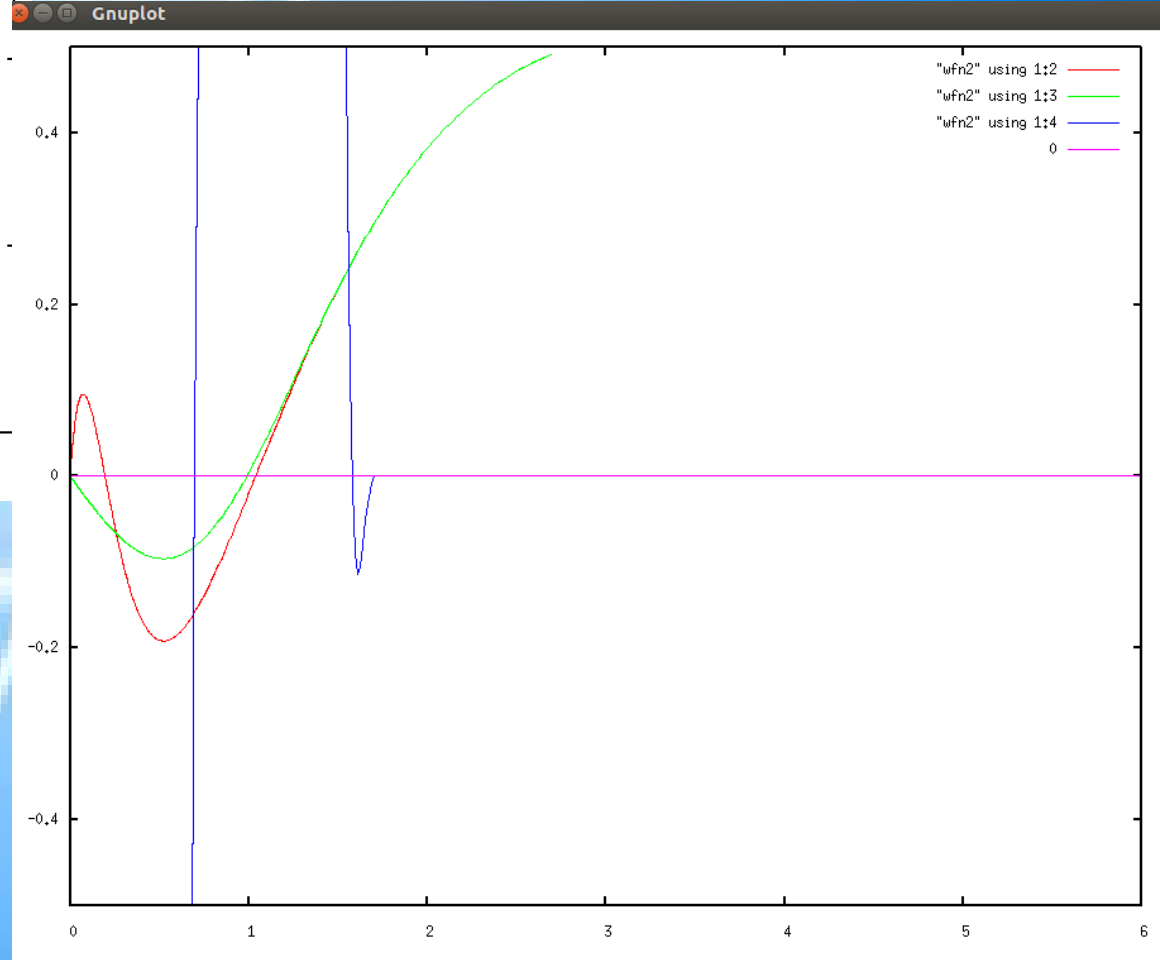
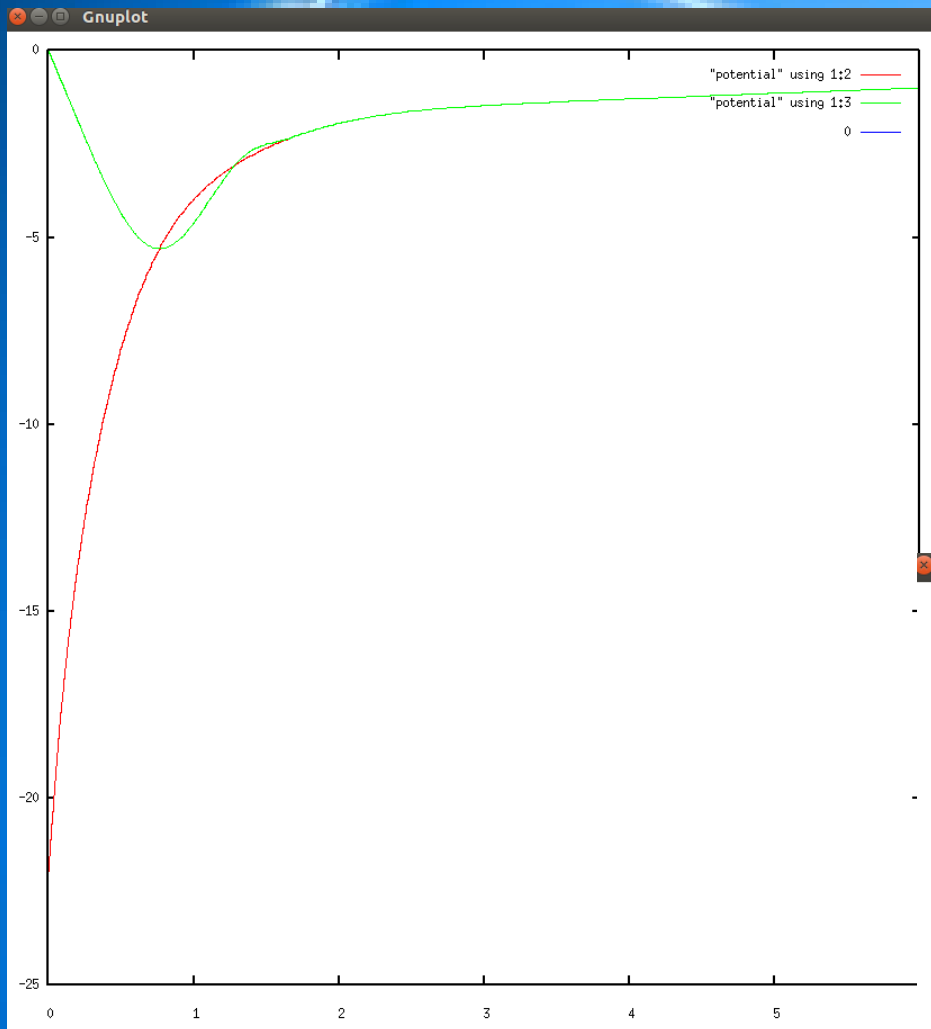
The computer program *atompaw* generates projector and basis functions which are needed for performing electronic structure calculations based on the Projector Augmented Wave (PAW) method. The program is applicable to materials throughout the periodic table. For each element, the user inputs the atomic number, the electronic configuration, a choice of basis functions, and an augmentation radius. The program produces an output file containing the projector and basis functions and the corresponding matrix elements in a form which can be read by the *pwpaw* PAW code. Additional data files are also produced which can be used to help evaluate the accuracy and efficiency of the generated functions. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 71.15.Ap; 71.15.Hx; 71.15.Mb; 71.15.Nc; 71.15.Pd; 2.70.c; 7.05.Tp

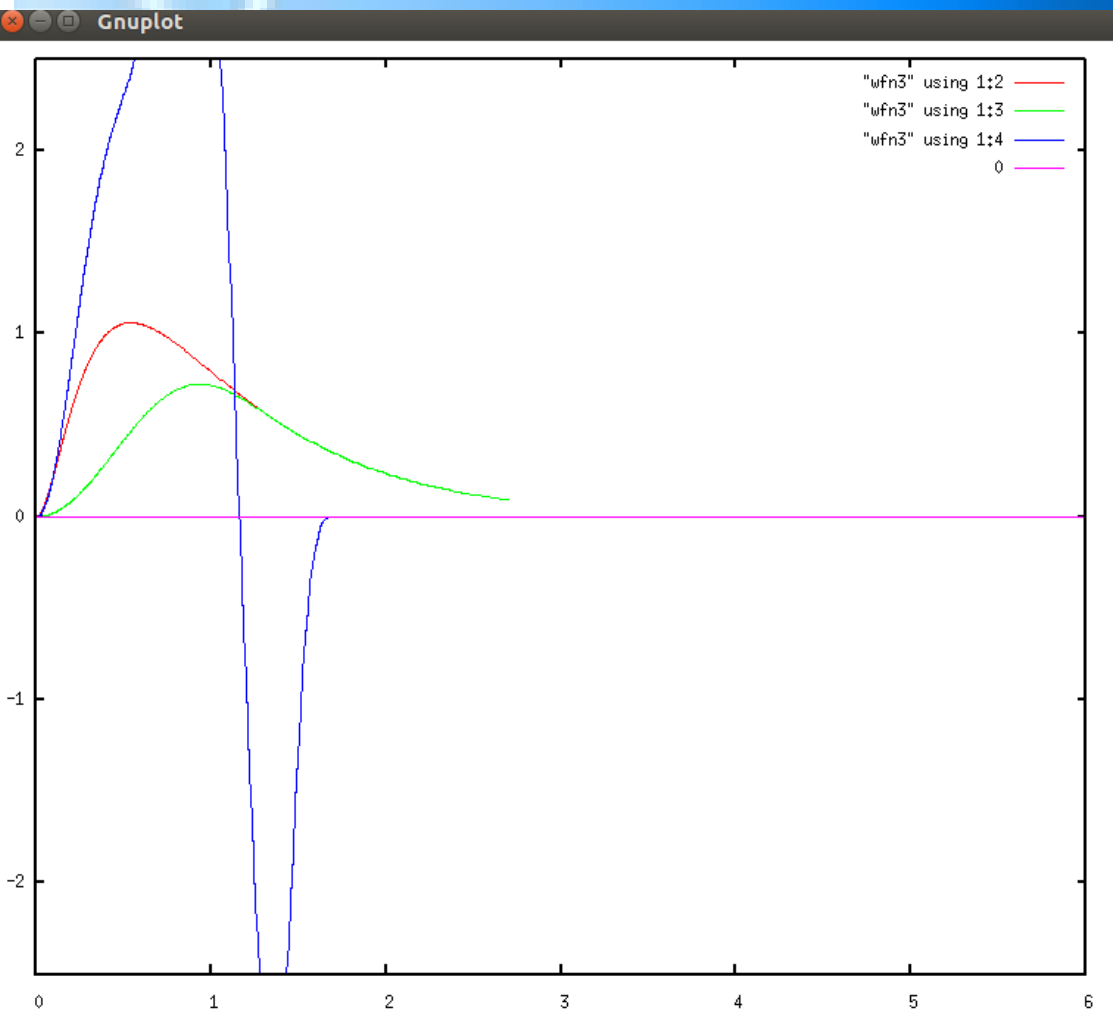
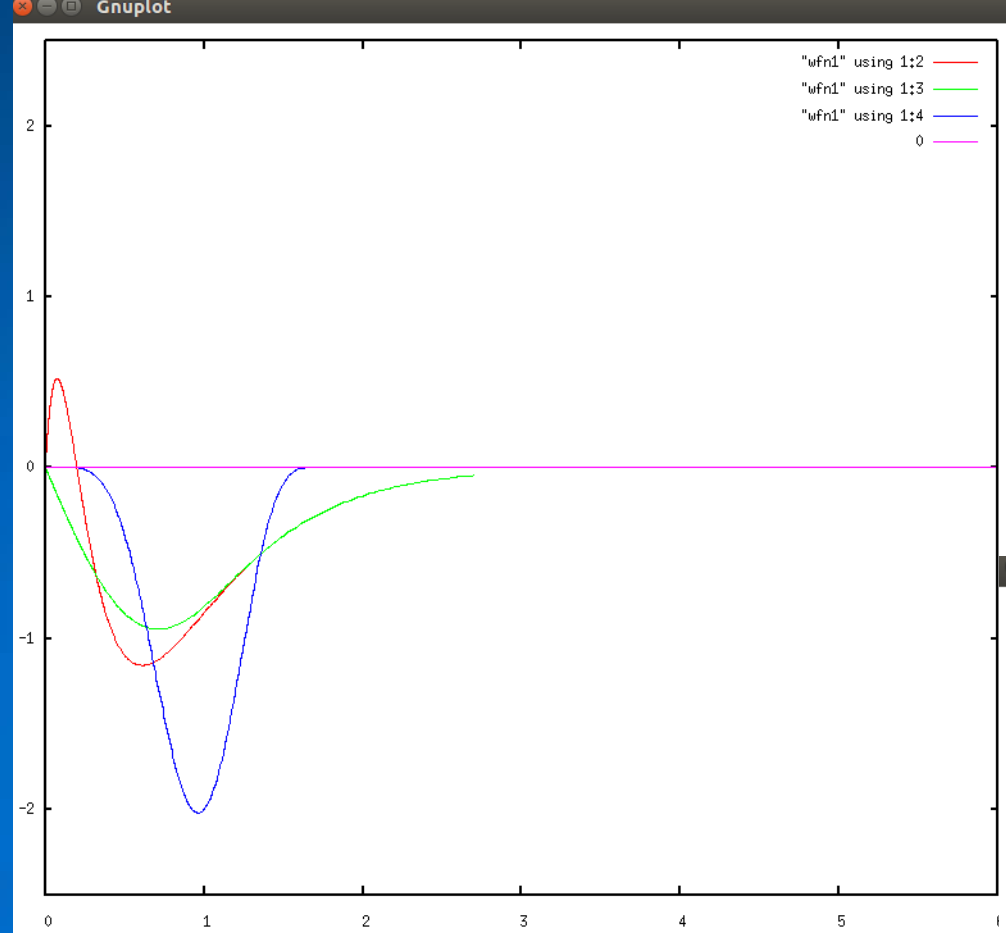
Keywords: Electronic structure calculations; Density functional calculation; Local density approximation; Projector Augmented Wave method; PAW; Computational methods

```
Na 11
LDA-PW loggridv4 2001
3 2 0 0 0 0
3 0 1
0 0 0
c
v
v
v
1
1.7 1.5 1.7 1.7
n
y
4.6
n
VANDERBILT Besselshape
2 0 MTROULLIER
1.5
1.7
1.5
1.7
XMLOUT
default
PWPAWOUT
ABINITOUT
default
PWSCFOUT
UPFDX 0.0125d0 UPFXMIN -7.d0 UPFZMESH 11.d0
END
```





6.02786 -06.0177



Na.LDA-PW-paw.UPF

<UPF version="2.0.1">

<PP_INFO>

UPF file from ATOMPAW code with following input

Na 11

LDA-PW loggridv4 2001

3 2 0 0 0

3 0 1

0 0 0

c

v

v

v

1

1.7 1.5 1.7 1.7

n

y

4.6

n

VANDERBILT Besselshape

2 0 MTROULLIER

<PP_MESH dx=" 1.2500000000000000E-02" mesh=" 969" xmin="-7.000000000000000E+00" zmesh=" 1.1000000000000000E+01">

<PP_R type="real" size=" 969" columns="3">

8.28983605049560246E-05 8.39410935153656594E-05 8.49969424924165604E-05

8.60660724146594458E-05 8.71486503358199859E-05 8.82448454109008079E-05

...

Effective core **pseudo**-potentials - ECP

rec	variable	value	meaning
• A	PSN		pseudo -potential keyword:
		HAYWLC	Hay and Wadt large core ECP.
		HAYWSC	Hay and Wadt small core ECP.
		BARTHE	Durand and Barthelat ECP.
		DURAND	Durand and Barthelat ECP.
		INPUT	free ECP - input follows.
			<i>if PSN = INPUT insert</i> _____ II
• *	ZNUC		effective core charge (ZN in eq. 2.16).
	M		Number of terms in eq. 2.17
	M0		Number of terms in eq. 2.18 for $\ell = 0$.
	M1		Number of terms in eq. 2.18 for $\ell = 1$.
	M2		Number of terms in eq. 2.18 for $\ell = 2$.
	M3		Number of terms in eq. 2.18 for $\ell = 3$.
	M4		Number of terms in eq. 2.18 for $\ell = 4$. - CRYSTAL09
			<i>insert $M+M0+M1+M2+M3+M4$ records</i> _____ II
• *	ALFKL		Exponents of the Gaussians: $\alpha_{k\ell}$.
	CGKL		Coefficient of the Gaussians: $C_{k\ell}$.
	NKL		Exponent of the r factors: $n_{k\ell}$.

Valence-electron only calculations can be performed with the aid of effective core pseudo-potentials (ECP). The ECP input must be inserted into the basis set input of the atoms with conventional atomic number > 200 .

The form of pseudo-potential W_{ps} implemented in *CRYSTAL* is a sum of three terms: a Coulomb term (C), a local term (W0) and a semi-local term (SL):

$$W_{ps} = C + W0 + SL \quad (2.15)$$

where:

$$C = -Z_N/r \quad (2.16)$$

$$W0 = \sum_{k=1}^M r^{n_k} C_k e^{-\alpha_k r^2} \quad (2.17)$$

$$SL = \sum_{\ell=0}^4 \left[\sum_{k=1}^{M_\ell} r^{n_{k\ell}} C_{k\ell} e^{-\alpha_{k\ell} r^2} \right] P_\ell \quad (2.18)$$

Z_N is the effective nuclear charge, equal to total nuclear charge minus the number of electrons represented by the ECP, P_ℓ is the projection operator related to the ℓ angular quantum number, and M , n_k , α_k , M_ℓ , $n_{k\ell}$, $C_{k\ell}$, $\alpha_{k\ell}$ are atomic pseudo-potential parameters.

Free input

228 5

INPUT

10.	5 4 5 2 0 0	
344.84100	-18.00000	-1
64.82281	-117.95937	0
14.28477	-29.43970	0
3.82101	-10.38626	0
1.16976	-0.89249	0
18.64238	3.00000	-2
4.89161	19.24490	-1
1.16606	23.93060	0
0.95239	-9.35414	0
30.60070	5.00000	-2
14.30081	19.81155	-1
15.03304	54.33856	0
4.64601	54.08782	0
0.98106	7.31027	0
4.56008	0.26292	0
0.67647	-0.43862	0
0 1 1 2. 1.		
1.257	1.	1.
0 1 1 0. 1.		
1.052	1.	1.
0 1 1 0. 1.		
0.0790	1.0	1.
0 3 4 8. 1.		
4.3580E+01	.03204	
1.1997E+01	.17577	
3.8938E+00	.41461	
1.271	.46122	
0 3 1 0. 1.		
0.385	1.	

Z=28, nickel basis set - 5 shells (valence only)

keyword: free ECP (Large Core)- input follows

nuclear charge; number of terms in eq. 2.17 and 2.18

eq. 2.17 5 records:

α , C, n

eq. 2.18 4 records $\ell = 0$

eq. 2.18 5 records $\ell = 1$

eq. 2.18 2 records $\ell = 2$

_____basis set input follows - valence only_____

1st shell: sp type; 1 GTF; CHE=2; scale fact.=1

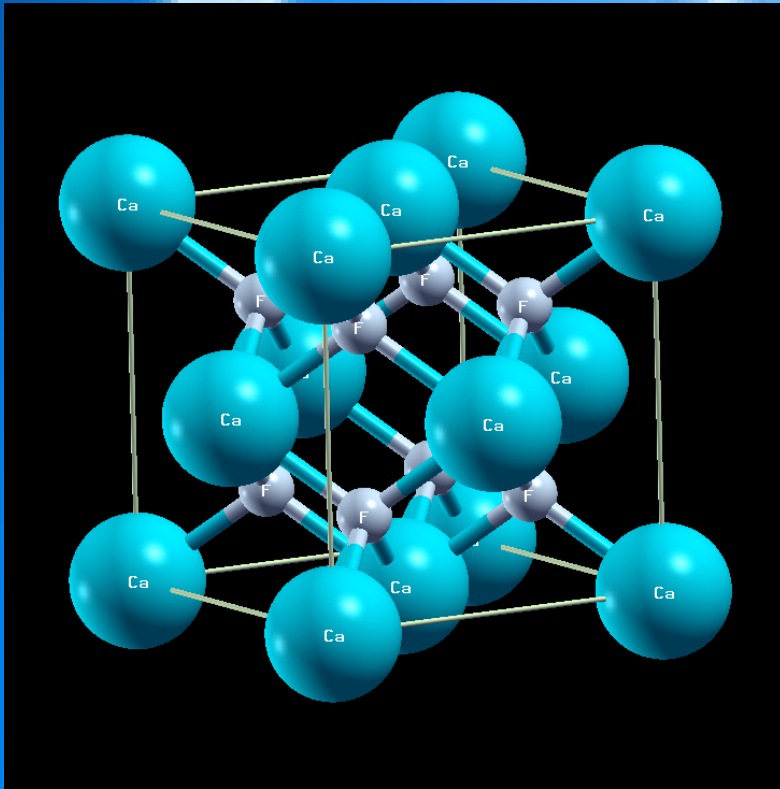
exponent, s coefficient, p coefficient

2nd shell: sp type; 1 GTF; CHE=0; scale fact.=1

3rd shell: sp type; 1 GTF; CHE=0; scale fact.=1

4th shell; d type; 4 GTF; CHE=8; scale fact.=1

5th shell; d type; 1 GTF; CHE=0; scale fact.=1



Ejemplo de cálculo con CRYSTAL
usando PS:

CaF₂, fluorita, Ca y F $a_{\text{exp}} = 5.462 \text{ \AA}$

Ca:

<http://www.crystal.unito.it/basis-sets.php>

Ca2+_SC-31G_doll_2010

A Kulkarni, K. Doll, J. C. Schoen, and M.
Jansen

Global Exploration of the Enthalpy
Landscape of Calcium Carbide

J. Phys. Chem. B 114, 15573 (2010)

based on the pseudopotential and basis set
from:

M. Kaupp, P. V. R. Schleyer, H. Stoll, H. Preuss, J. Chem. Phys. 94, 1360 (1991)

F:

F_7-311G_nada_1993

R. Nada, C.R.A. Catlow, C. Pisani and R. Orlando,

``Ab initio Hartree-Fock perturbed-cluster study of neutral defects in LiF'',
Modelling. Simul. Mater. Sci. Eng. 1, 165-187 (1993).

Input:

Caf2

CRYSTAL

0 0 0

225

5.46 5.46 5.46 90. 90. 90.

2

220 0. 0. 0.

9 .25 .25 .25

OPTGEOM

CELLONLY

ENDOPT

END

220 5

INPUT

10. 0 2 2 2 1 0

11.231672 138.785174 0

4.671960 16.504244 0

11.156907 83.123664 0

4.810141 13.502272 0

13.754728 -16.201965 0

4.762470 -1.132390 0

12.765846 -26.728178 0

0 0 3 2.0 1

12.3075210 0.0587400

4.3931510 -0.4013440

0.9379750 0.5928750

0 0 1 0.0 1

0.4216880 1.0

0 0 1 0.0 1

0.2 1.0

0 2 3 6.0 1

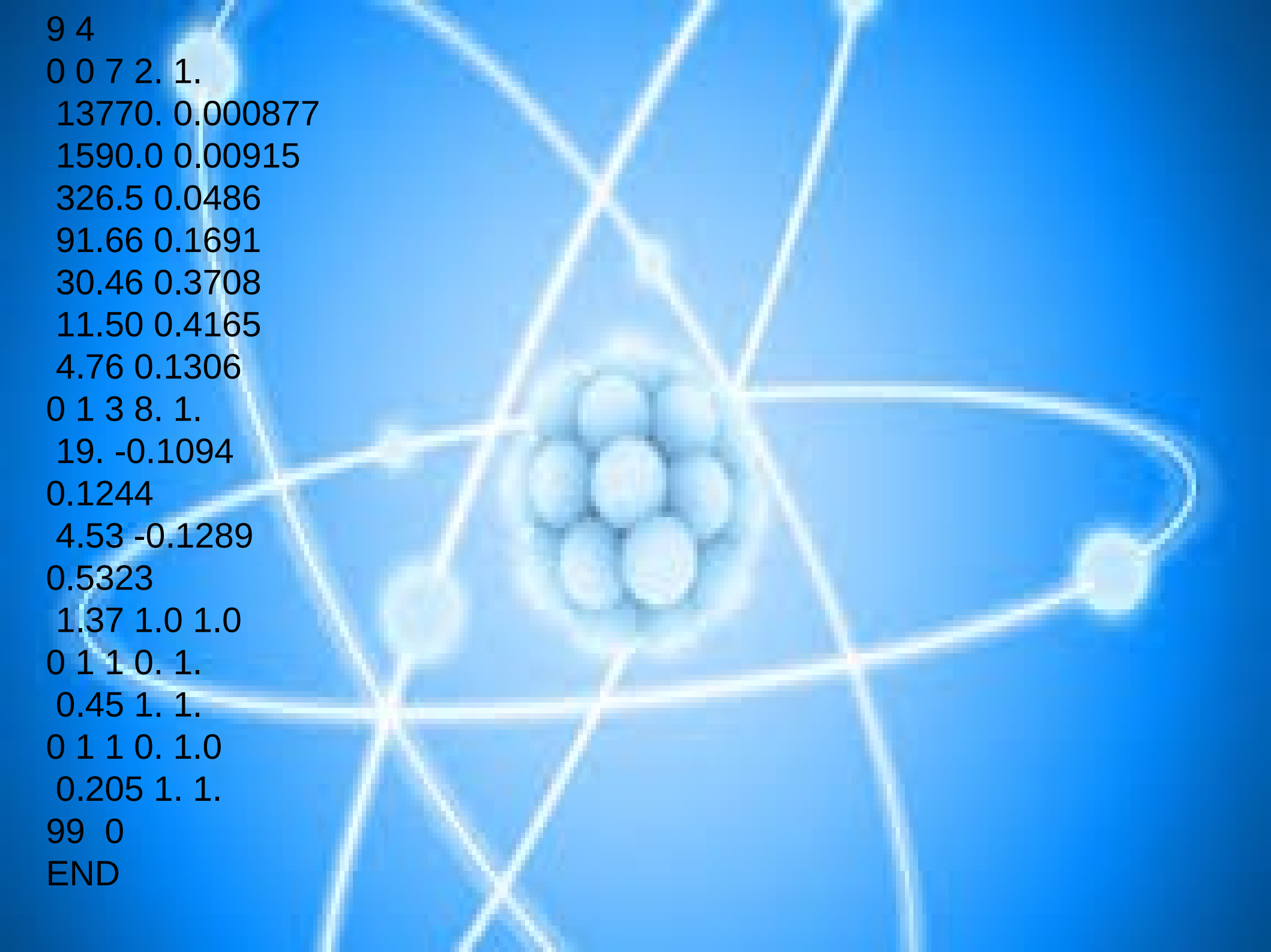
5.9742860 -0.0823020

1.5674060 0.3465110

0.6562420 0.5601470

0 2 1 .0 1

0.2584980 1.0



```
9 4
0 0 7 2. 1.
13770. 0.000877
1590.0 0.00915
326.5 0.0486
91.66 0.1691
30.46 0.3708
11.50 0.4165
4.76 0.1306
0 1 3 8. 1.
19. -0.1094
0.1244
4.53 -0.1289
0.5323
1.37 1.0 1.0
0 1 1 0. 1.
0.45 1. 1.
0 1 1 0. 1.0
0.205 1. 1.
99 0
END
```



```
DFT
SPIN
HSEsol
ENDdft
FMIXING
85
TOLDEE
7
LEVSHIFT
2
1
MAXCYCLE
2000
SPINLOCK
0 300
SHRINK
0 1
4 4 4
MULPOPAN
BIPOSIZE
2500000
EXCHSIZE
2810000
END
```

Resultados

opt: $a_{\text{calc}} = 5.52875073 \text{ \AA}$

MULLIKEN POPULATION ANALYSIS - NO. OF
ELECTRONS 28.000000

ATOM Z CHARGE A.O. POPULATION

1	CA	220	8.084	0.825	1.121	0.105	1.651	1.651	1.651
			0.360	0.360					
				0.360					
2	F	9	9.958	1.999	0.835	1.048	1.048	1.048	0.860
			0.523	0.523					
				0.523	0.311	0.414	0.414	0.414	
3	F	9	9.958	1.999	0.835	1.048	1.048	1.048	0.860
			0.523	0.523					
				0.523	0.311	0.414	0.414	0.414	

