HybriD^3 Theory Training Workshop -- organized by Y. Kanai (UNC) and V. Blum (Duke)

Practical Density Functional Theory with Plane Waves)

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- Cameron Kates, Jamie Drewery, Hannah Zhang, Zachary Pipkorn (former WFU undergrads)
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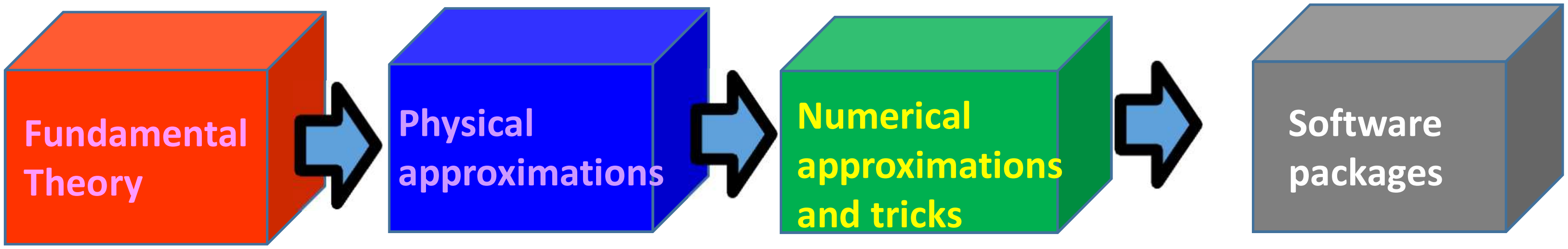
- NSF grant DMR-1507942

Perspectives on Materials Simulations


Fundamental Theory

Physical approximations

Numerical approximations and tricks

Software packages


input parameters

quantum-espresso (http://www.quantum-espresso.org/)

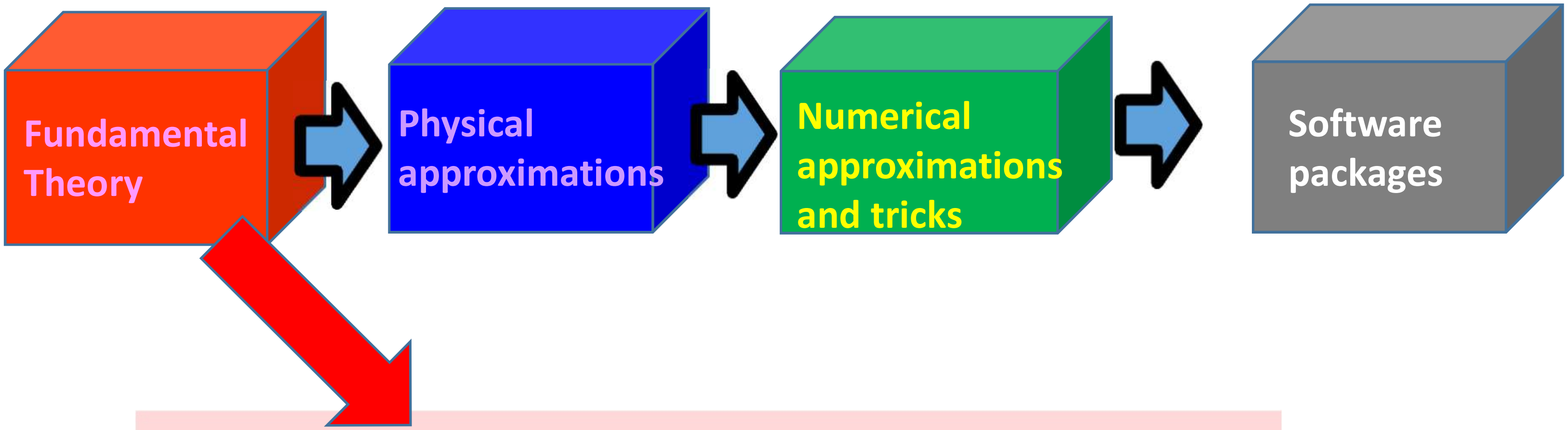
abinit (https://www.abinit.org/)

Qbox (http://qboxcode.org/)

FHI-aims (https://aimsclub.fhi-berlin.mpg.de/)

useful results

It is important to know what is inside the box!



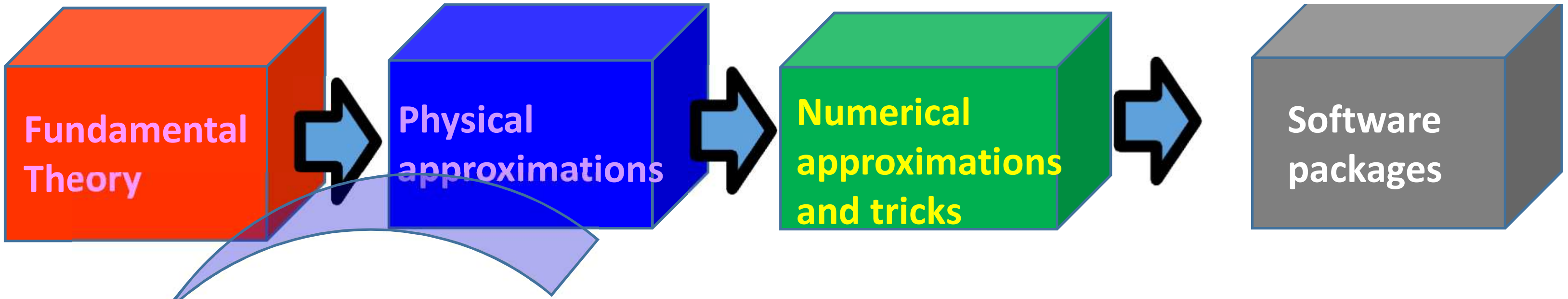
Fundamental Theory

Physical approximations

Numerical approximations and tricks

Software packages

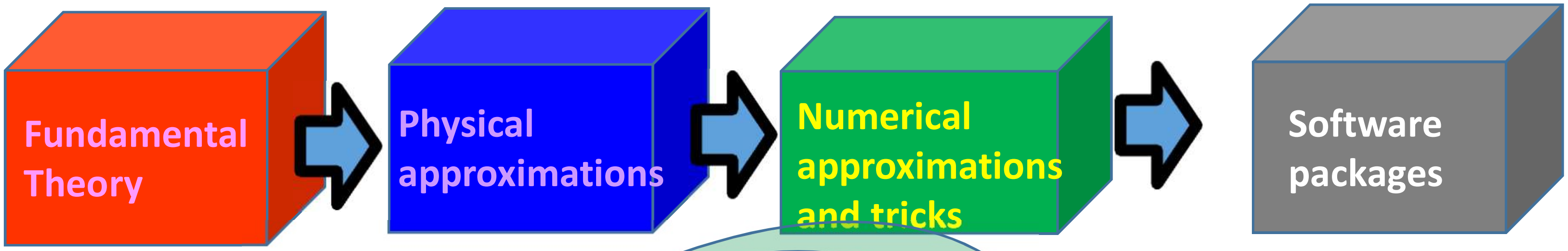
Quantum mechanics and electrodynamics as it applies to many particle systems



Born-Oppenheimer approximation [*Born & Huang, Dynamical Theory of Crystal Lattices , Oxford (1954)*]: Nuclear motions treated classically while electronic motions treated quantum mechanically because $M_N >> m_e$

Density functional theory [*Kohn, Hohenberg, Sham, PR 136, B864 (1964), PR 140, A1133 (1965)*]: Many electron system approximated by single particle approximation using a self-consistent mean field.

Frozen core approximation[*von Barth, Gelatt, PRB 21, 2222 (1980)*]: Core electrons assumed to be “frozen” at their atomic values; valence electrons evaluated variationally.



Fundamental Theory

Physical approximations

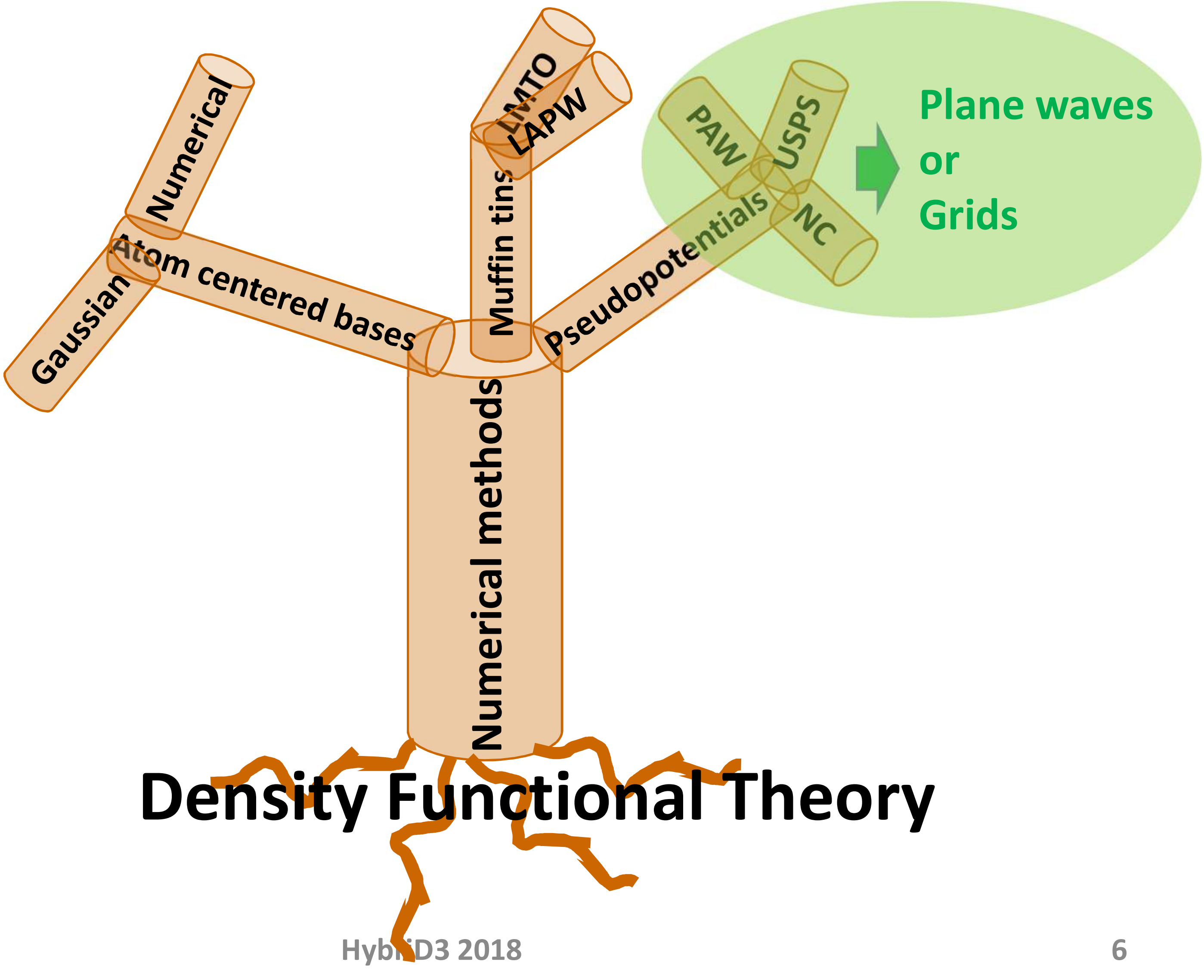
Numerical approximations and tricks

Software packages

Plane wave representations of electronic wavefunctions and densities

Pseudopotential formulations

Numerical methods more generally --



Plane waves
or
Grids

Practical Density Functional Theory with Plane Waves)

Outline

- Treatment of core and valence electrons; frozen core approximation
- Use of plane wave expansions in materials simulations
- Pseudopotentials
  - Norm conserving pseudopotentials
  - Projector augmented wave formalism
- Assessment of the calculations

Summary and conclusions:

- Materials simulations is a mature field; there are many great ideas to use, but there still is plenty of room for innovation.
- Maintain a skeptical attitude to the literature and to your own results.
- Introduce checks into your work. For example, perform at least two independent calculations for a representative sample.
- On balance, static lattice results seem to be under good control. The next frontier is more accurate treatment of thermal effects and other aspects of representing macroscopic systems.
- Developing first-principles models of real materials to understand and predict their properties continues to challenge computational scientists.

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Practical Density Functional Theory with Plane Waves)

Outline

- Treatment of core and valence electrons; frozen core approximation
- Use of plane wave expansions in materials simulations
- Pseudopotentials
  - Norm conserving pseudopotentials
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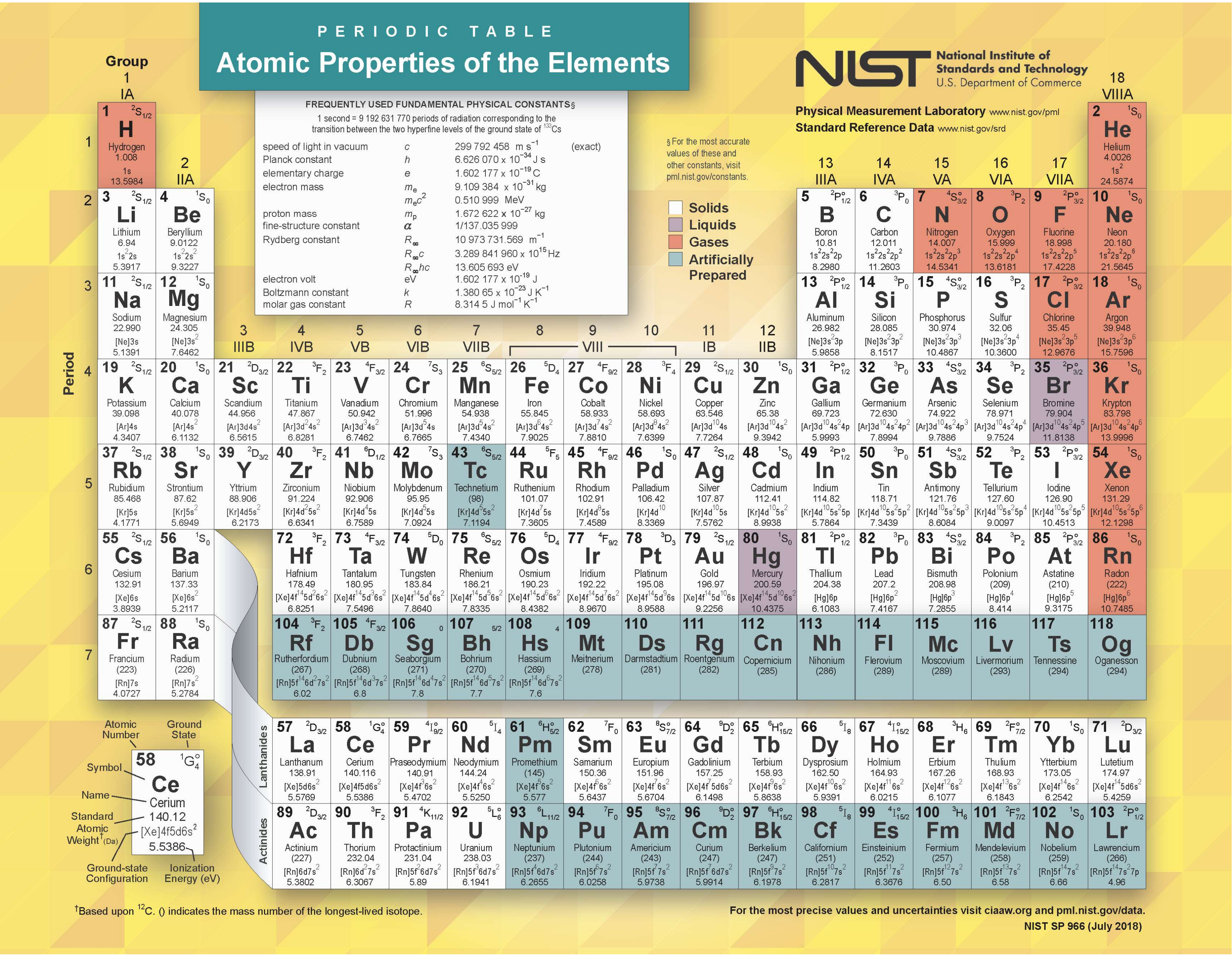


PERIODIC TABLE

Atomic Properties of the Elements

National Institute of Standards and Technology
U.S. Department of Commerce

Physical Measurement Laboratory www.nist.gov/pml
Standard Reference Data www.nist.gov/srd

FREQUENTLY USED FUNDAMENTAL PHYSICAL CONSTANTS§

1 second = 9 192 631 770 periods of radiation corresponding to the transition between the two hyperfine levels of the ground state of ^{133}Cs

speed of light in vacuum	c	299 792 458 m s^{-1}	(exact)
Planck constant	h	6.626 070 x 10^{-34} J s	
elementary charge	e	1.602 177 x 10^{-19} C	
electron mass	m_e	9.109 384 x 10^{-31} kg	
	m_ec^2	0.510 999 MeV	
proton mass	m_p	1.672 622 x 10^{-27} kg	
fine-structure constant	α	1/137.035 999	
Rydberg constant	R_∞	10 973 731.569 m^{-1}	
	$R_\infty c$	3.289 841 960 x 10^{15} Hz	
	$R_\infty hc$	13.605 693 eV	
electron volt	eV	1.602 177 x 10^{-19} J	
Boltzmann constant	k	1.380 65 x 10^{-23} J K^{-1}	
molar gas constant	R	8.314 5 J mol^{-1} K^{-1}	

§ For the most accurate values of these and other constants, visit pml.nist.gov/constants.

☐ Solids
🟪 Liquids
🟥 Gases
🟦 Artificially Prepared

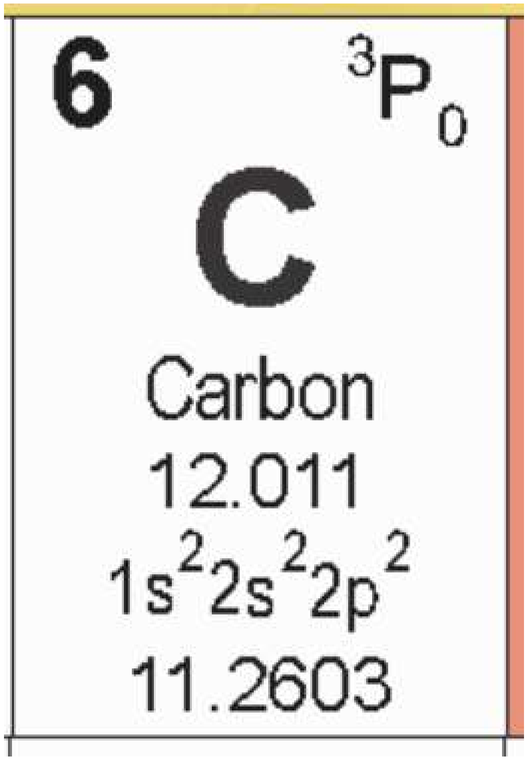
Atomic Number	Ground State	Symbol	Name	Standard Atomic Weight† (Da)	Ground-state Configuration	Ionization Energy (eV)
1	$^2S_{1/2}$	H	Hydrogen	1.008	$1s$	13.5984
2	$^1S_0$	He	Helium	4.0026	$1s^2$	24.5874
3	$^2S_{1/2}$	Li	Lithium	6.94	$1s^2 2s$	5.3917
4	$^1S_0$	Be	Beryllium	9.0122	$1s^2 2s^2$	9.3227
5	$^2P^\circ_{1/2}$	B	Boron	10.81	$1s^2 2s^2 2p$	8.2980
6	$^3P_0$	C	Carbon	12.011	$1s^2 2s^2 2p^2$	11.2603
7	$^4S^\circ_{3/2}$	N	Nitrogen	14.007	$1s^2 2s^2 2p^3$	14.5341
8	$^3P_2$	O	Oxygen	15.999	$1s^2 2s^2 2p^4$	13.6181
9	$^2P^\circ_{3/2}$	F	Fluorine	18.998	$1s^2 2s^2 2p^5$	17.4228
10	$^1S_0$	Ne	Neon	20.180	$1s^2 2s^2 2p^6$	21.5645
11	$^2S_{1/2}$	Na	Sodium	22.990	[Ne]$3s$	5.1391
12	$^1S_0$	Mg	Magnesium	24.305	[Ne]$3s^2$	7.6462
13	$^2P^\circ_{1/2}$	Al	Aluminum	26.982	[Ne]$3s^2 3p$	5.9858
14	$^3P_0$	Si	Silicon	28.085	[Ne]$3s^2 3p^2$	8.1517
15	$^4S^\circ_{3/2}$	P	Phosphorus	30.974	[Ne]$3s^2 3p^3$	10.4867
16	$^3P_2$	S	Sulfur	32.06	[Ne]$3s^2 3p^4$	10.3600
17	$^2P^\circ_{3/2}$	Cl	Chlorine	35.45	[Ne]$3s^2 3p^5$	12.9676
18	$^1S_0$	Ar	Argon	39.948	[Ne]$3s^2 3p^6$	15.7596
19	$^2S_{1/2}$	K	Potassium	39.098	[Ar]$4s$	4.3407
20	$^1S_0$	Ca	Calcium	40.078	[Ar]$4s^2$	6.1132
21	$^2D_{3/2}$	Sc	Scandium	44.956	[Ar]$3d4s^2$	6.5615
22	$^3F_2$	Ti	Titanium	47.867	[Ar]$3d^2 4s^2$	6.8281
23	$^4F_{3/2}$	V	Vanadium	50.942	[Ar]$3d^3 4s^2$	6.7462
24	$^7S_3$	Cr	Chromium	51.996	[Ar]$3d^5 4s$	6.7665
25	$^6S_{5/2}$	Mn	Manganese	54.938	[Ar]$3d^5 4s^2$	7.4340
26	$^5D_4$	Fe	Iron	55.845	[Ar]$3d^6 4s^2$	7.9025
27	$^4F_{9/2}$	Co	Cobalt	58.933	[Ar]$3d^7 4s^2$	7.8810
28	$^3F_4$	Ni	Nickel	58.693	[Ar]$3d^8 4s^2$	7.6399
29	$^2S_{1/2}$	Cu	Copper	63.546	[Ar]$3d^{10} 4s$	7.7264
30	$^1S_0$	Zn	Zinc	65.38	[Ar]$3d^{10} 4s^2$	9.3942
31	$^2P^\circ_{1/2}$	Ga	Gallium	69.723	[Ar]$3d^{10} 4s^2 4p$	5.9993
32	$^3P_0$	Ge	Germanium	72.630	[Ar]$3d^{10} 4s^2 4p^2$	7.8994
33	$^4S^\circ_{3/2}$	As	Arsenic	74.922	[Ar]$3d^{10} 4s^2 4p^3$	9.7886
34	$^3P_2$	Se	Selenium	78.971	[Ar]$3d^{10} 4s^2 4p^4$	9.7524
35	$^2P^\circ_{3/2}$	Br	Bromine	79.904	[Ar]$3d^{10} 4s^2 4p^5$	11.8138
36	$^1S_0$	Kr	Krypton	83.798	[Ar]$3d^{10} 4s^2 4p^6$	13.9996
37	$^2S_{1/2}$	Rb	Rubidium	85.468	[Kr]$5s$	4.1771
38	$^1S_0$	Sr	Strontium	87.62	[Kr]$5s^2$	5.6949
39	$^2D_{3/2}$	Y	Yttrium	88.906	[Kr]$4d5s^2$	6.2173
40	$^3F_2$	Zr	Zirconium	91.224	[Kr]$4d^2 5s^2$	6.6341
41	$^6D_{1/2}$	Nb	Niobium	92.906	[Kr]$4d^4 5s$	6.7589
42	$^7S_3$	Mo	Molybdenum	95.95	[Kr]$4d^5 5s$	7.0924
43	$^6S_{5/2}$	Tc	Technetium	(98)	[Kr]$4d^5 5s^2$	7.1194
44	$^5F_5$	Ru	Ruthenium	101.07	[Kr]$4d^7 5s$	7.3605
45	$^4F_{9/2}$	Rh	Rhodium	102.91	[Kr]$4d^8 5s$	7.4589
46	$^1S_0$	Pd	Palladium	106.42	[Kr]$4d^{10}$	8.3369
47	$^2S_{1/2}$	Ag	Silver	107.87	[Kr]$4d^{10} 5s$	7.5762
48	$^1S_0$	Cd	Cadmium	112.41	[Kr]$4d^{10} 5s^2$	8.9938
49	$^2P^\circ_{1/2}$	In	Indium	114.82	[Kr]$4d^{10} 5s^2 5p$	5.7864
50	$^3P_0$	Sn	Tin	118.71	[Kr]$4d^{10} 5s^2 5p^2$	7.3439
51	$^4S^\circ_{3/2}$	Sb	Antimony	121.76	[Kr]$4d^{10} 5s^2 5p^3$	8.6084
52	$^3P_2$	Te	Tellurium	127.60	[Kr]$4d^{10} 5s^2 5p^4$	9.0097
53	$^2P^\circ_{3/2}$	I	Iodine	126.90	[Kr]$4d^{10} 5s^2 5p^5$	10.4513
54	$^1S_0$	Xe	Xenon	131.29	[Kr]$4d^{10} 5s^2 5p^6$	12.1298
55	$^2S_{1/2}$	Cs	Cesium	132.91	[Xe]$6s$	3.8939
56	$^1S_0$	Ba	Barium	137.33	[Xe]$6s^2$	5.2117
57	$^2D_{3/2}$	La	Lanthanum	138.91	[Xe]$5d6s^2$	5.5769
58	$^1G^\circ_4$	Ce	Cerium	140.116	[Xe]$4f5d6s^2$	5.5386
59	$^4I^\circ_{9/2}$	Pr	Praseodymium	140.91	[Xe]$4f^3 6s^2$	5.4702
60	$^5I_4$	Nd	Neodymium	144.24	[Xe]$4f^4 6s^2$	5.5250
61	$^6H^\circ_{5/2}$	Pm	Promethium	(145)	[Xe]$4f^5 6s^2$	5.577
62	$^7F_0$	Sm	Samarium	150.36	[Xe]$4f^6 6s^2$	5.6437
63	$^8S^\circ_{7/2}$	Eu	Europium	151.96	[Xe]$4f^7 6s^2$	5.6704
64	$^9D^\circ_2$	Gd	Gadolinium	157.25	[Xe]$4f^7 5d6s^2$	6.1498
65	$^6H^\circ_{15/2}$	Tb	Terbium	158.93	[Xe]$4f^9 6s^2$	5.8638
66	$^5I_8$	Dy	Dysprosium	162.50	[Xe]$4f^{10} 6s^2$	5.9391
67	$^4I^\circ_{15/2}$	Ho	Holmium	164.93	[Xe]$4f^{11} 6s^2$	6.0215
68	$^3H_6$	Er	Erbium	167.26	[Xe]$4f^{12} 6s^2$	6.1077
69	$^2F^\circ_{7/2}$	Tm	Thulium	168.93	[Xe]$4f^{13} 6s^2$	6.1843
70	$^1S_0$	Yb	Ytterbium	173.05	[Xe]$4f^{14} 6s^2$	6.2542
71	$^2D_{3/2}$	Lu	Lutetium	174.97	[Xe]$4f^{14} 5d6s^2$	5.4259
72	$^3F_2$	Hf	Hafnium	178.49	[Xe]$4f^{14} 5d^2 6s^2$	6.8251
73	$^4F_{3/2}$	Ta	Tantalum	180.95	[Xe]$4f^{14} 5d^3 6s^2$	7.5496
74	$^5D_0$	W	Tungsten	183.84	[Xe]$4f^{14} 5d^4 6s^2$	7.8640
75	$^6S_{5/2}$	Re	Rhenium	186.21	[Xe]$4f^{14} 5d^5 6s^2$	7.8335
76	$^5D_4$	Os	Osmium	190.23	[Xe]$4f^{14} 5d^6 6s^2$	8.4382
77	$^4F_{9/2}$	Ir	Iridium	192.22	[Xe]$4f^{14} 5d^7 6s^2$	8.9670
78	$^3D_3$	Pt	Platinum	195.08	[Xe]$4f^{14} 5d^9 6s$	8.9588
79	$^2S_{1/2}$	Au	Gold	196.97	[Xe]$4f^{14} 5d^{10} 6s$	9.2256
80	$^1S_0$	Hg	Mercury	200.59	[Xe]$4f^{14} 5d^{10} 6s^2$	10.4375
81	$^2P^\circ_{1/2}$	Tl	Thallium	204.38	[Hg]$6p$	6.1083
82	$^3P_0$	Pb	Lead	207.2	[Hg]$6p^2$	7.4167
83	$^4S^\circ_{3/2}$	Bi	Bismuth	208.98	[Hg]$6p^3$	7.2855
84	$^3P_2$	Po	Polonium	(209)	[Hg]$6p^4$	8.414
85	$^2P^\circ_{3/2}$	At	Astatine	(210)	[Hg]$6p^5$	9.3175
86	$^1S_0$	Rn	Radon	(222)	[Hg]$6p^6$	10.7485
87	$^2S_{1/2}$	Fr	Francium	(223)	[Rn]$7s$	4.0727
88	$^1S_0$	Ra	Radium	(226)	[Rn]$7s^2$	5.2784
89	$^2D_{3/2}$	Ac	Actinium	(227)	[Rn]$6d7s^2$	5.3802
90	$^3F_2$	Th	Thorium	232.04	[Rn]$6d^2 7s^2$	6.3067
91	$^4K_{11/2}$	Pa	Protactinium	231.04	[Rn]$5f^2 6d7s^2$	5.89
92	$^5L^\circ_6$	U	Uranium	238.03	[Rn]$5f^3 6d7s^2$	6.1941
93	$^6L_{11/2}$	Np	Neptunium	(237)	[Rn]$5f^4 6d7s^2$	6.2655
94	$^7F_0$	Pu	Plutonium	(244)	[Rn]$5f^6 7s^2$	6.0258
95	$^8S^\circ_{7/2}$	Am	Americium	(243)	[Rn]$5f^7 7s^2$	5.9738
96	$^9D^\circ_2$	Cm	Curium	(247)	[Rn]$5f^7 6d7s^2$	5.9914
97	$^6H^\circ_{15/2}$	Bk	Berkelium	(247)	[Rn]$5f^9 7s^2$	6.1978
98	$^5I_8$	Cf	Californium	(251)	[Rn]$5f^{10} 7s^2$	6.2817
99	$^4I^\circ_{15/2}$	Es	Einsteinium	(252)	[Rn]$5f^{11} 7s^2$	6.3676
100	$^3H_6$	Fm	Fermium	(257)	[Rn]$5f^{12} 7s^2$	6.50
101	$^2F^\circ_{7/2}$	Md	Mendelevium	(258)	[Rn]$5f^{13} 7s^2$	6.58
102	$^1S_0$	No	Nobelium	(259)	[Rn]$5f^{14} 7s^2$	6.66
103	$^2P^\circ_{1/2}$	Lr	Lawrencium	(266)	[Rn]$5f^{14} 7s^2 7p$	4.96
104	$^3F_2$	Rf	Rutherfordium	(267)	[Rn]$5f^{14} 6d^2 7s^2$	6.02
105	$^4F_{3/2}$	Db	Dubnium	(268)	[Rn]$5f^{14} 6d^3 7s^2$	6.8
106	$_0$	Sg	Seaborgium	(271)	[Rn]$5f^{14} 6d^4 7s^2$	7.8
107	$_{5/2}$	Bh	Bohrium	(270)	[Rn]$5f^{14} 6d^5 7s^2$	7.7
108	$_4$	Hs	Hassium	(269)	[Rn]$5f^{14} 6d^6 7s^2$	7.6
109		Mt	Meitnerium	(278)		
110		Ds	Darmstadtium	(281)		
111		Rg	Roentgenium	(282)		
112		Cn	Copernicium	(285)		
113		Nh	Nihonium	(286)		
114		Fl	Flerovium	(289)		
115		Mc	Moscovium	(289)		
116		Lv	Livermorium	(293)		
117		Ts	Tennessine	(294)		
118		Og	Oganesson	(294)		

†Based upon ^{12}C. () indicates the mass number of the longest-lived isotope.

For the most precise values and uncertainties visit ciaaw.org and pml.nist.gov/data.

NIST SP 966 (July 2018)

Two examples --



6 $^{3}P_{0}$

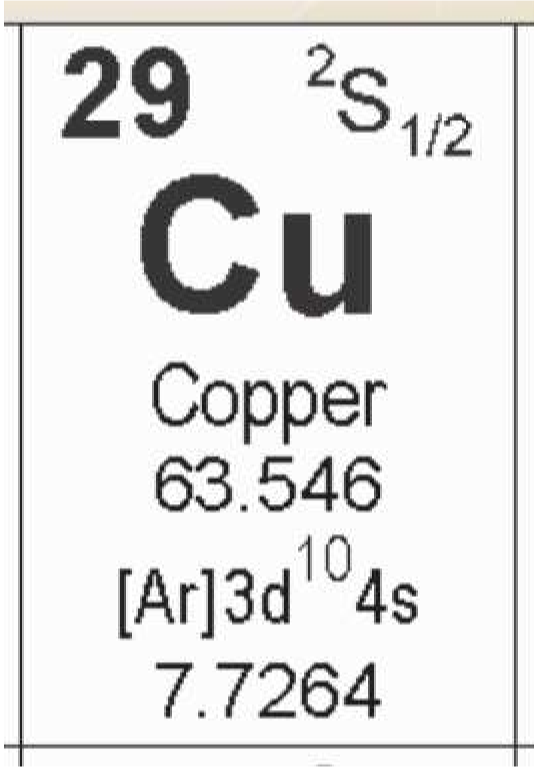
C

Carbon

12.011

$1s^{2}2s^{2}2p^{2}$

11.2603



29 $^{2}S_{1/2}$

Cu

Copper

63.546

$[Ar]3d^{10}4s$

7.7264

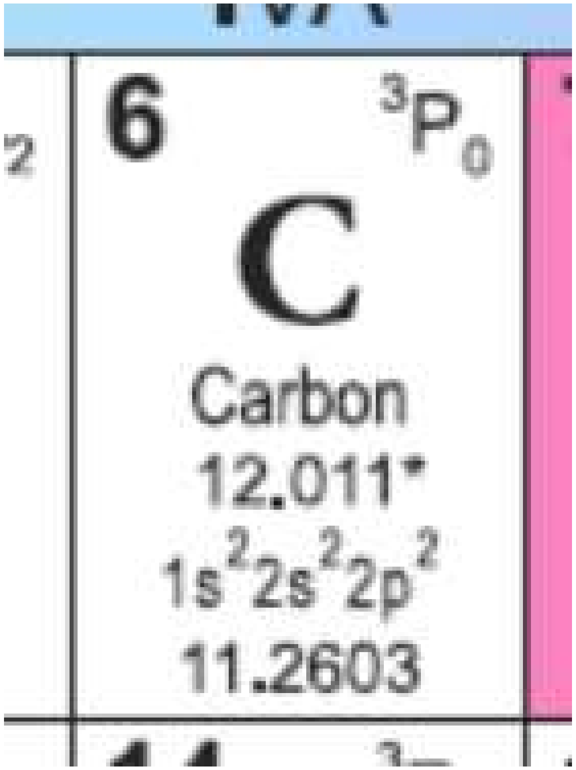
Partitioning electrons into core and valence contributions

$$n(r) = n_{core}(r) + n_{vale}(r)$$

For spherically symmetric atom:

$$\phi_{n_i l_i m_i}(\mathbf{r}) = \phi_{n_i l_i}(r) Y_{l_i m_i}(\hat{\mathbf{r}})$$

$$\phi_{n_i l_i}(r) = \frac{P_{n_i l_i}(r)}{r}$$



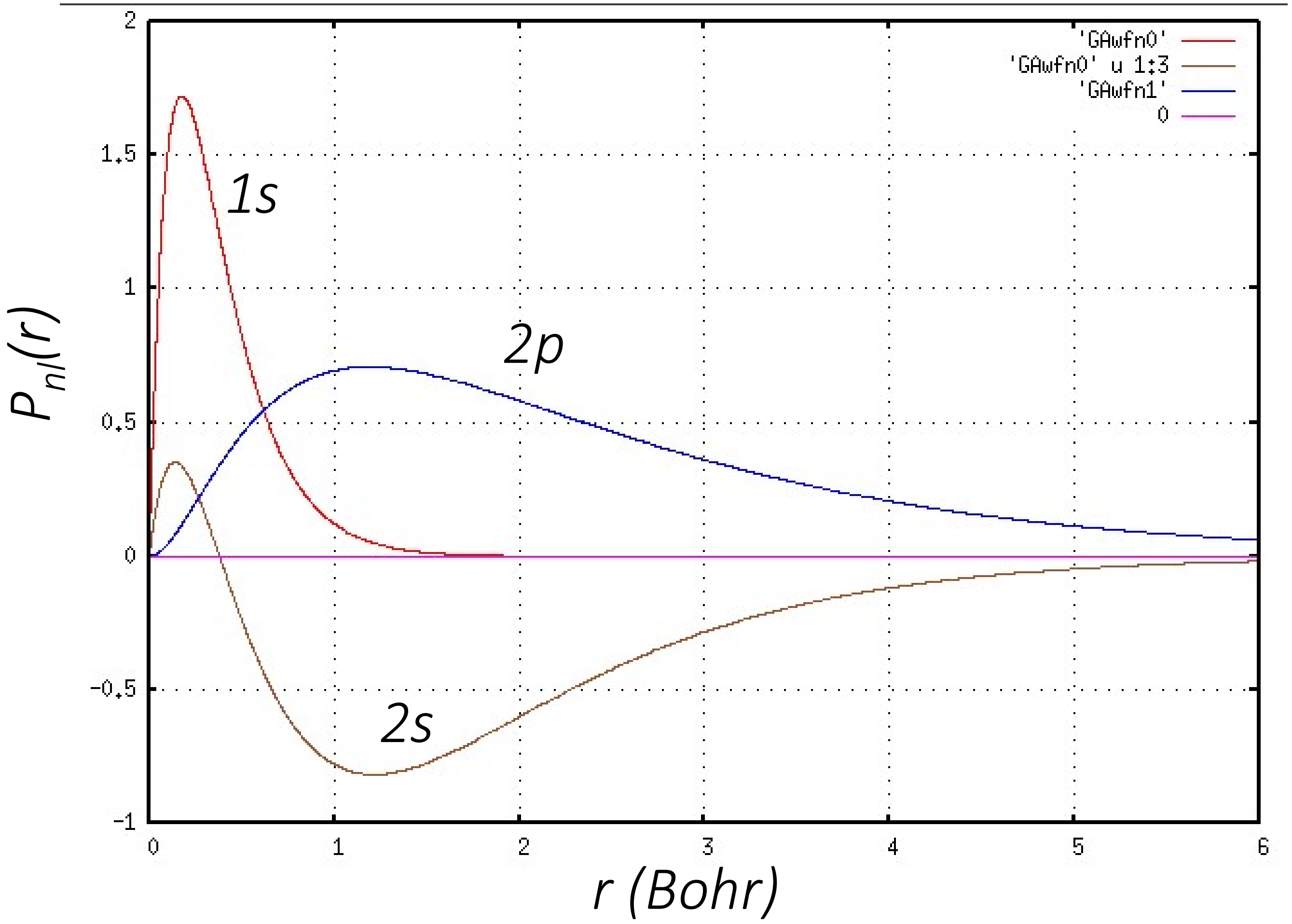
Example for carbon

$$n(r) = \sum_i w_{n_i l_i} \left|\phi_{n_i l_i}(r)\right|^2$$

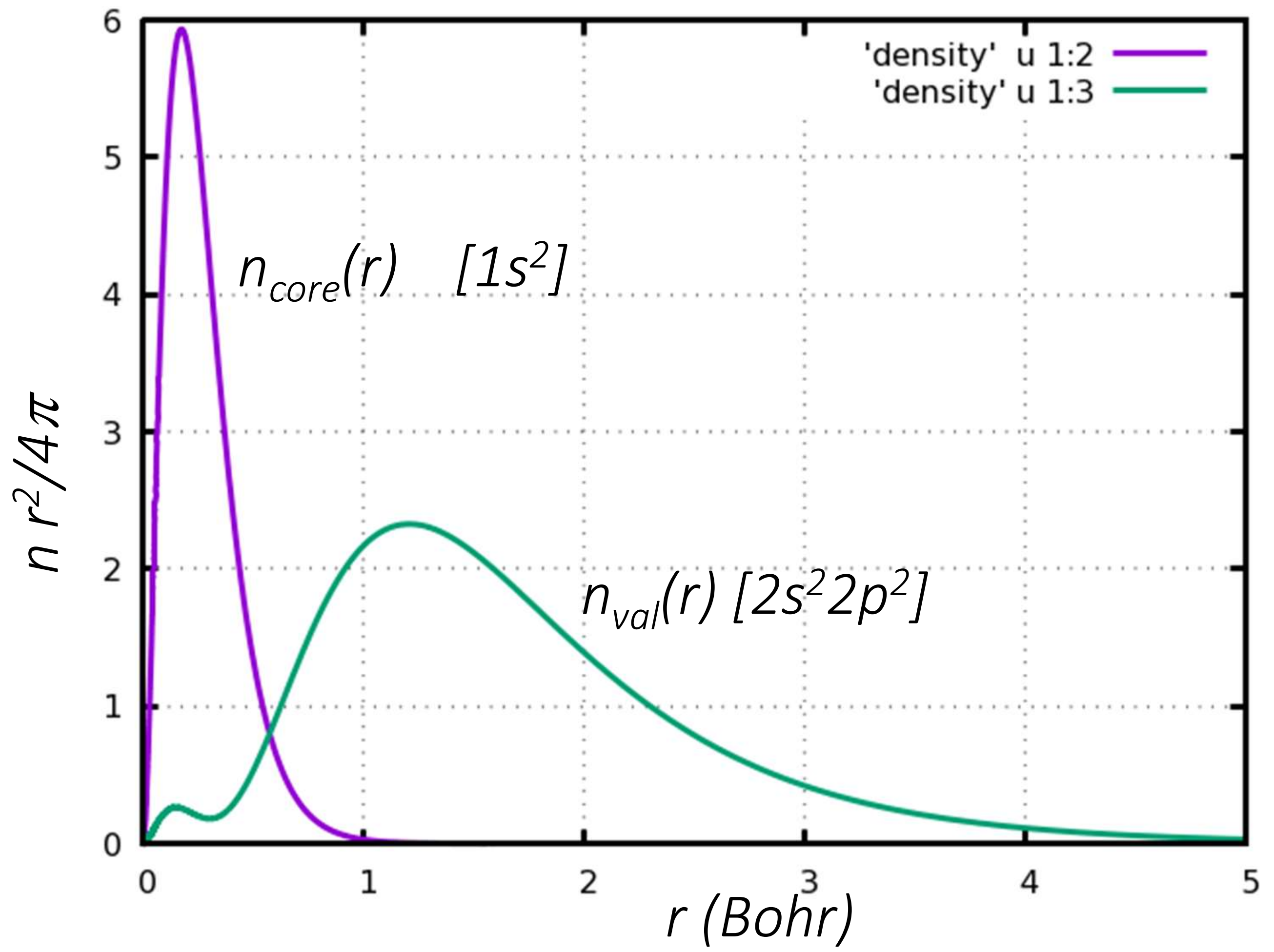
$$= 4\pi \left(2\left|\phi_{1s}(r)\right|^2 + 2\left|\phi_{2s}(r)\right|^2 + 2\left|\phi_{2p}(r)\right|^2 \right)$$

$$= \frac{4\pi}{r^2} \left(2\left|P_{1s}(r)\right|^2 + 2\left|P_{2s}(r)\right|^2 + 2\left|P_{2p}(r)\right|^2 \right)$$

Radial wavefunctions for carbon



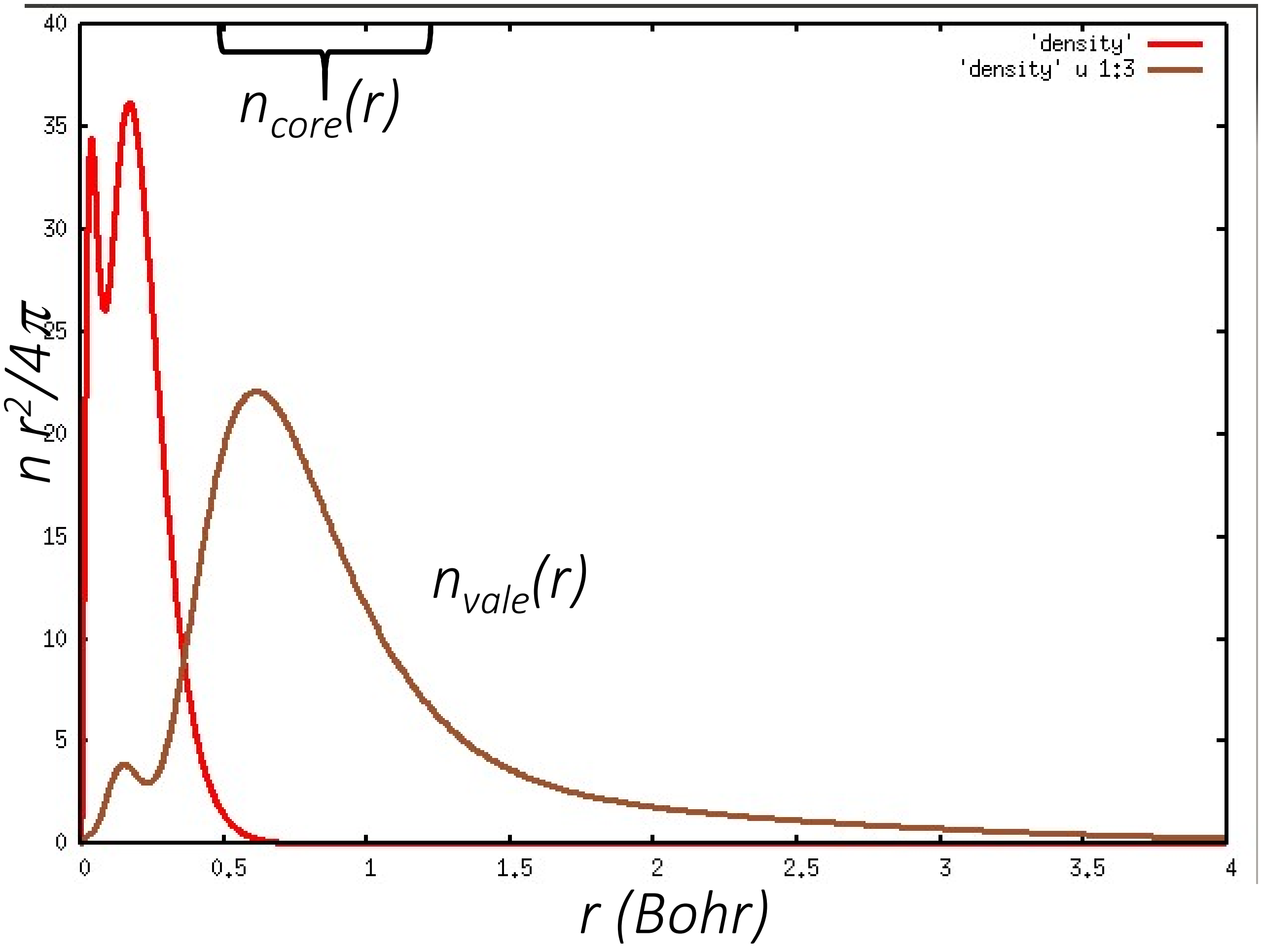
Electron density of C atom

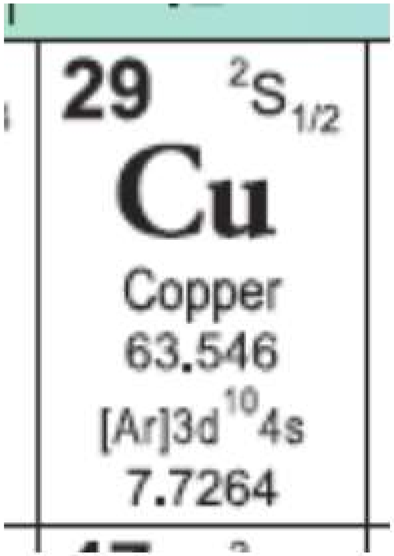


Electron density of copper

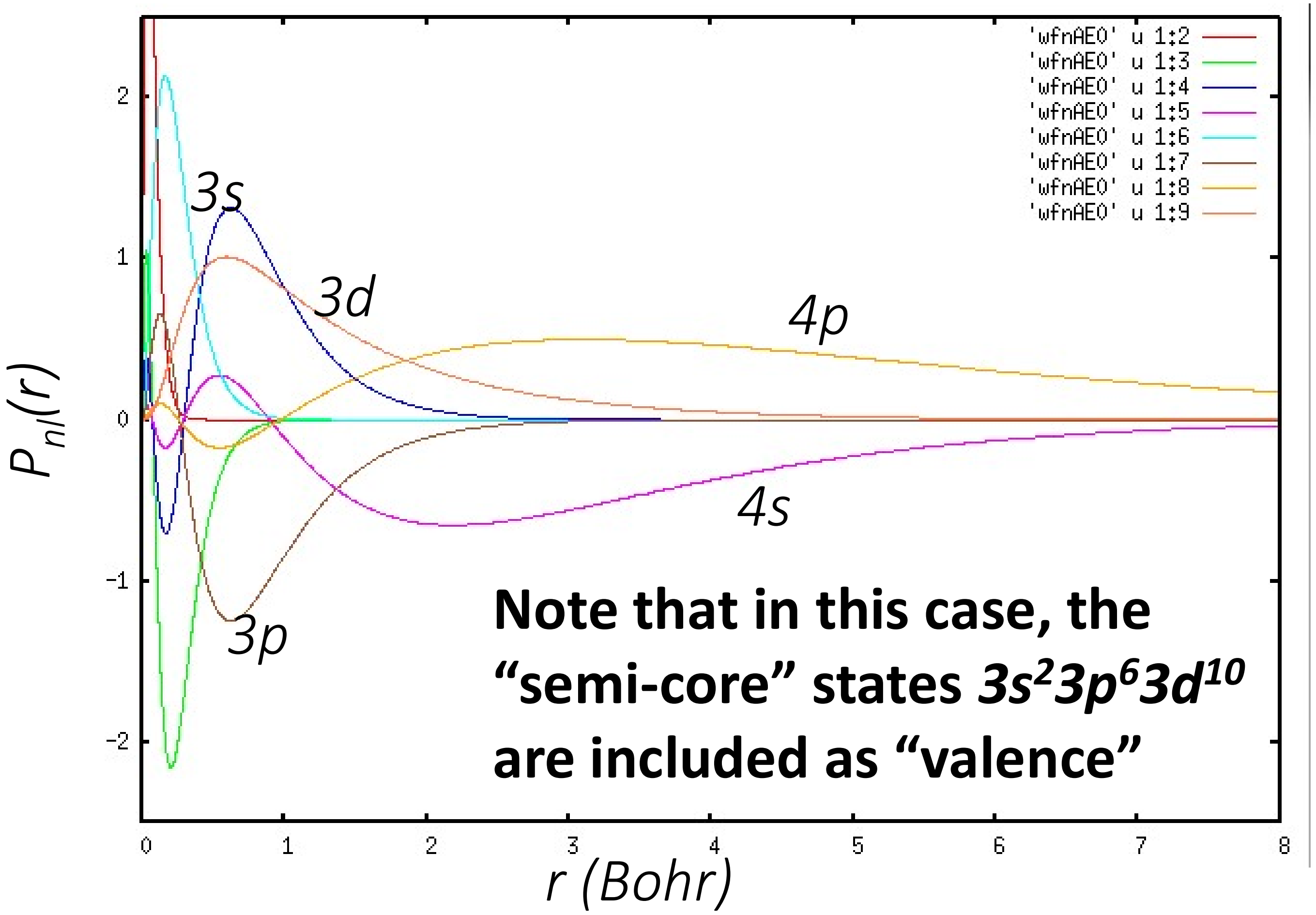
Example for Cu

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$





Radial wavefunctions for Cu



Note that in this case, the “semi-core” states $3s^2 3p^6 3d^{10}$ are included as “valence”

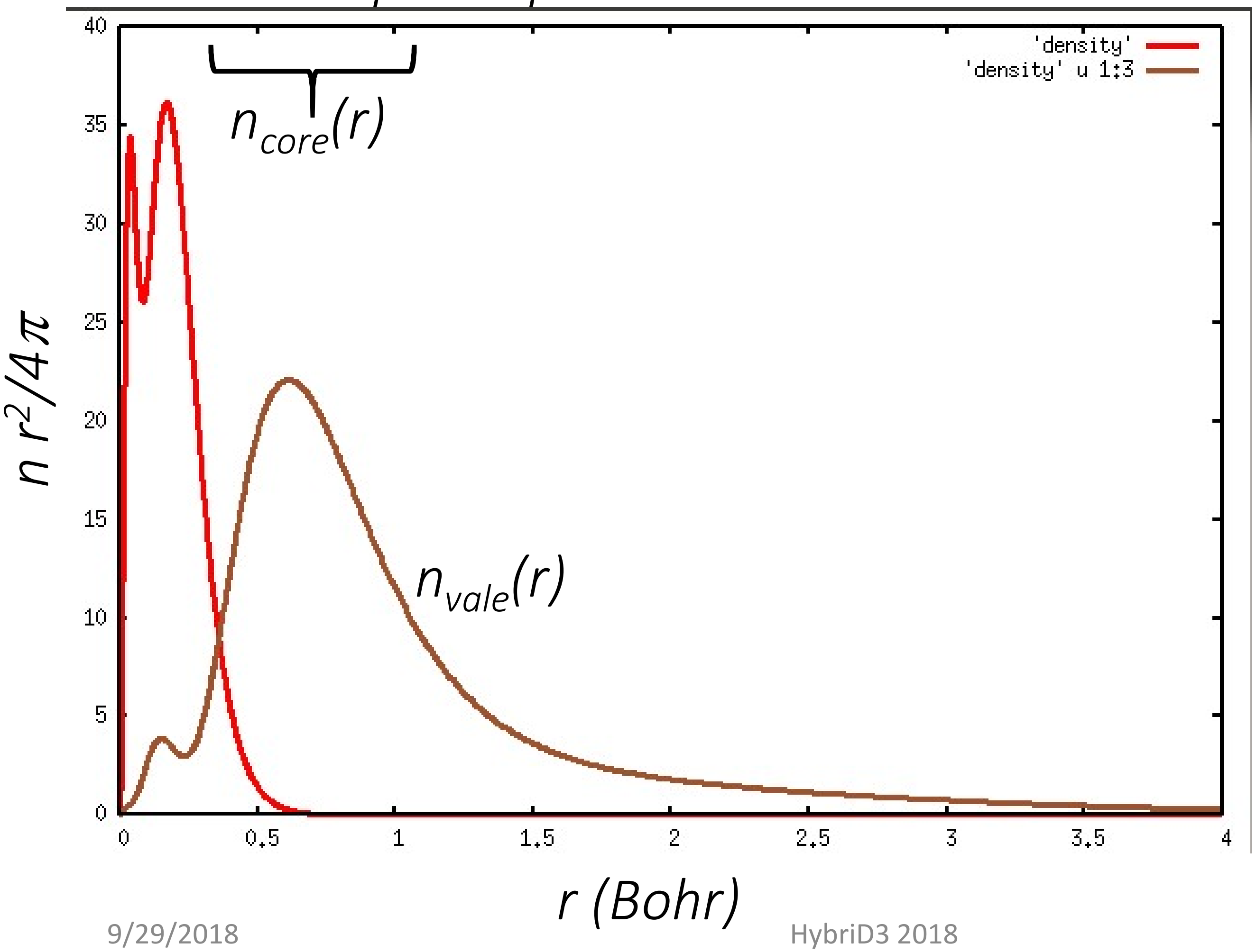
Frozen core approximation

$$n(r) = n_{\text{core}}(r) + n_{\text{vale}}(r)$$

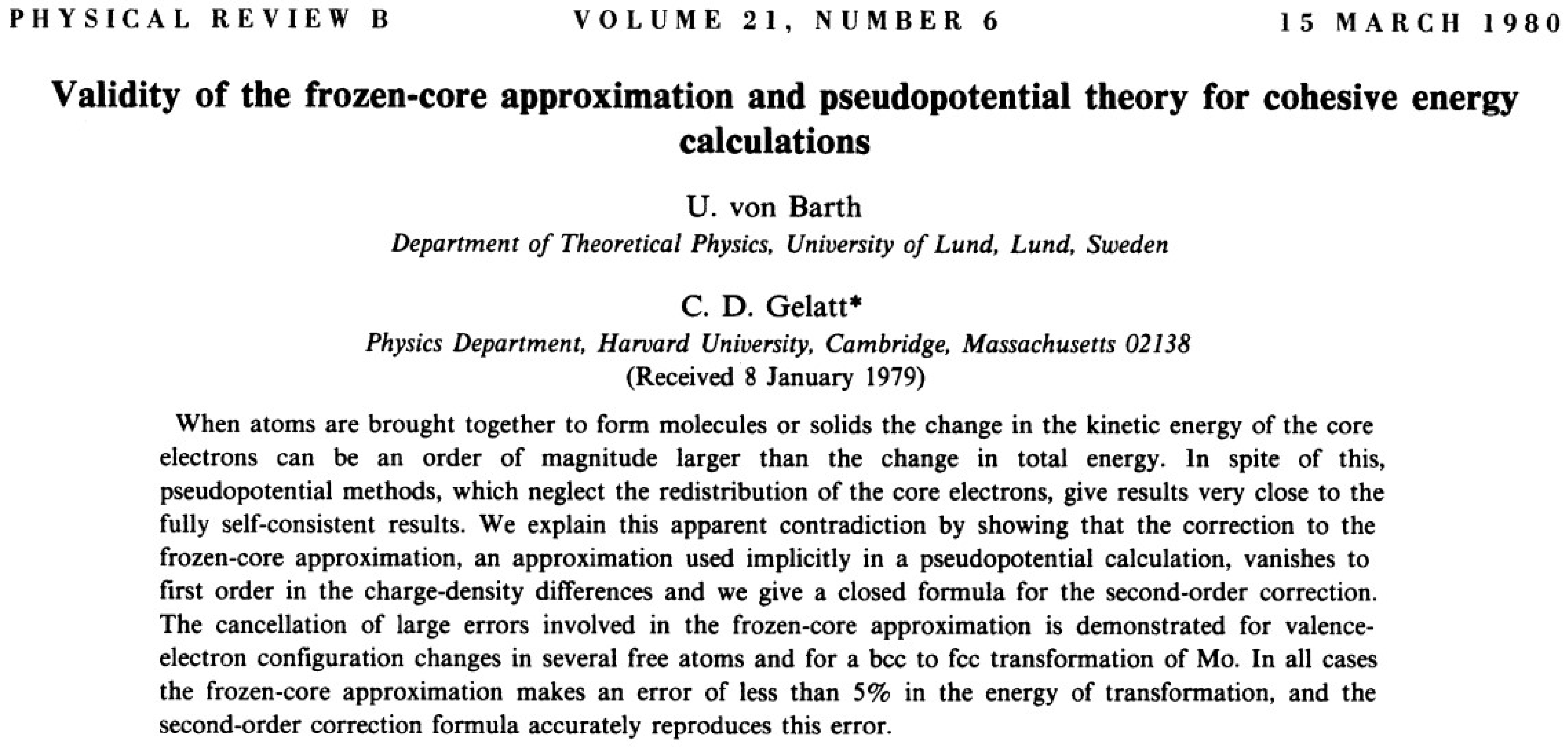
Example for Cu

Variationally optimize energy wrt $n_{\text{vale}}(r)$

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$



Systematic study of frozen core approximation in DFT



PHYSICAL REVIEW B VOLUME 21, NUMBER 6 15 MARCH 1980

Validity of the frozen-core approximation and pseudopotential theory for cohesive energy calculations

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(Received 8 January 1979)

When atoms are brought together to form molecules or solids the change in the kinetic energy of the core electrons can be an order of magnitude larger than the change in total energy. In spite of this, pseudopotential methods, which neglect the redistribution of the core electrons, give results very close to the fully self-consistent results. We explain this apparent contradiction by showing that the correction to the frozen-core approximation, an approximation used implicitly in a pseudopotential calculation, vanishes to first order in the charge-density differences and we give a closed formula for the second-order correction. The cancellation of large errors involved in the frozen-core approximation is demonstrated for valence-electron configuration changes in several free atoms and for a bcc to fcc transformation of Mo. In all cases the frozen-core approximation makes an error of less than 5% in the energy of transformation, and the second-order correction formula accurately reproduces this error.

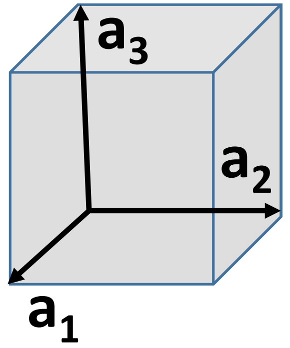
http://journals.aps.org/prb/abstract/10.1103/PhysRevB.21.2222

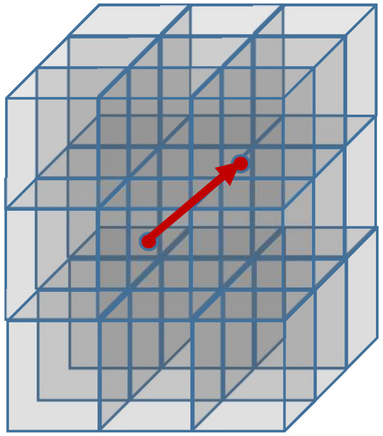
Practical Density Functional Theory with Plane Waves)

Outline

- Treatment of core and valence electrons; frozen core approximation
- **Use of plane wave expansions in materials simulations**
- Pseudopotentials
  - Norm conserving pseudopotentials
  - Projector augmented wave formalism
- Assessment of the calculations

Consider a periodic material with a unit cell described by primitive lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$:





Multiple unit cells

Any position $\mathbf{r}$ in the material is related to an infinite number of other points in the material $\mathbf{r}+\mathbf{T} \equiv \mathbf{r}+n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3$ because of its periodic symmetry.

Because of Bloch's theorem, any wavefunction of the system having wavevector $\mathbf{k}$, has the property: $\Psi_{\mathbf{k}}(\mathbf{r}+\mathbf{T}) = e^{i\mathbf{k}\cdot\mathbf{T}}\Psi_{\mathbf{k}}(\mathbf{r})$. This means that $\Psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r})$, where $u_{\mathbf{k}}(\mathbf{r})$ is a periodic function.

All directly measurable properties of the system also reflect the periodic nature of the system. For example, the electron density: $n(\mathbf{r}+\mathbf{T}) = n(\mathbf{r})$

Mathematical relationships – The Fourier transform of a periodic function results in a discrete summation based on the reciprocal lattice.

For the electron density: $n(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{n}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$, where $\mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$

The reciprocal lattice vectors are related to the primitive translation

vectors according to $\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$; $\mathbf{b}_i = 2\pi \dfrac{\mathbf{a}_j \times \mathbf{a}_k}{\mathbf{a}_i \cdot (\mathbf{a}_j \times \mathbf{a}_k)}$

Here $\tilde{n}(\mathbf{G}) = \dfrac{1}{\Omega} \int_{\text{unit cell}} d^3r \; e^{-i\mathbf{G}\cdot\mathbf{r}} n(\mathbf{r})$.

$\Rightarrow$ Fourier transforms are a natural basis for periodic functions.

For example, the periodic part of the Bloch wave function:

$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{u}_{\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$ and $\Psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{u}_{\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$

This works well, provided the summation converges in the sense

that $|\tilde{u}_{\mathbf{k}}(\mathbf{G})| < \epsilon$ for $|\mathbf{k}+\mathbf{G}| > K_{\max}$.

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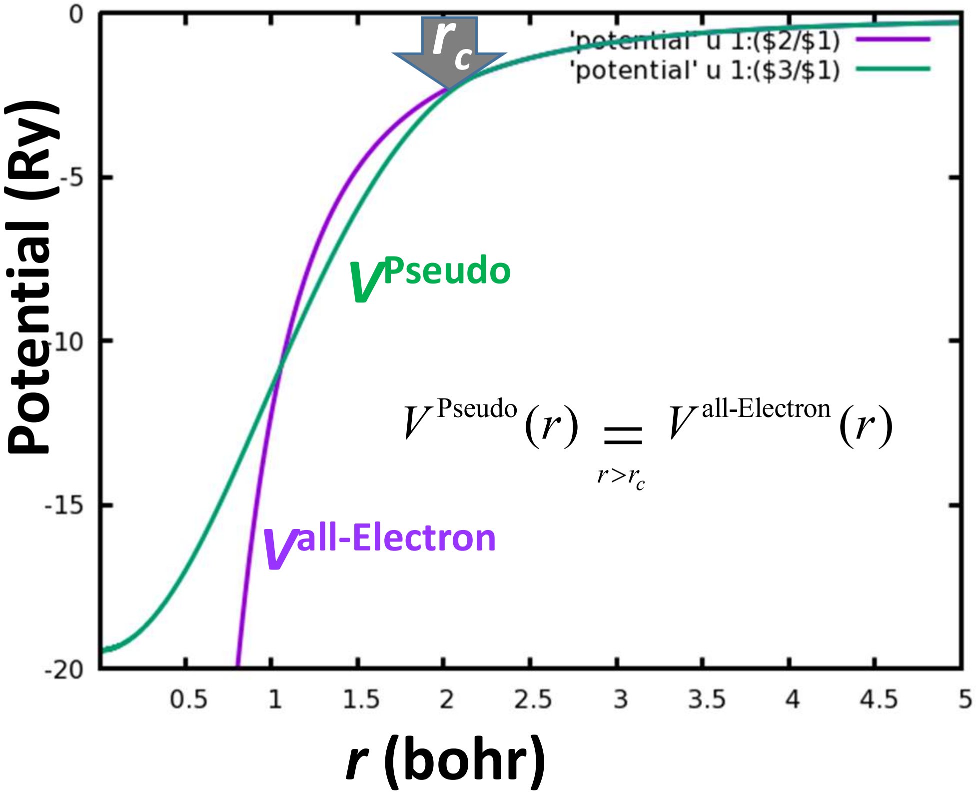
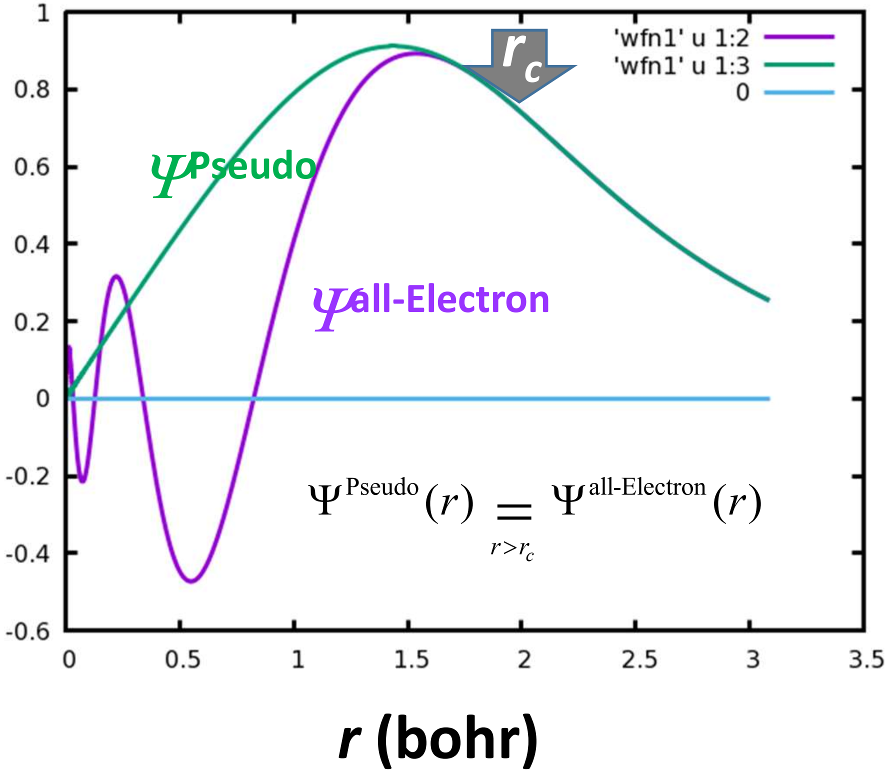
- **Pseudopotentials**
  - **Norm conserving pseudopotentials**
  - **Projector augmented wave formalism**
- Assessment of the calculations

The notion of pseudopotential has been attributed To Enrico Fermi in the 1930's. "First principles" pseudopotentials were developed by Hamann, Schlüter, and Chiang, PRL 43, 1494 (1979) and J. Kerker, J. Phys. C 13, L189 (1980).



Cs effective potential

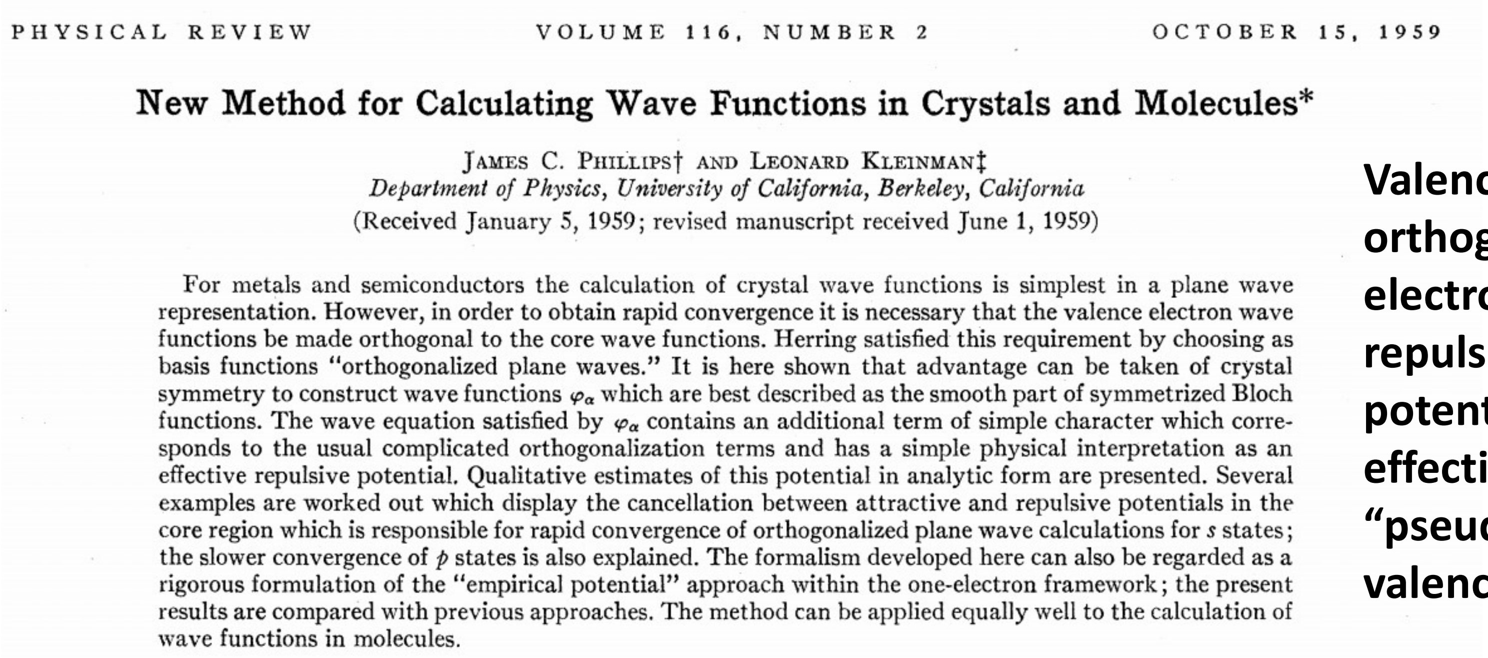
$$V^{\text{Pseudo}}(r) \underset{r>r_c}{=} V^{\text{all-Electron}}(r)$$



Cs *5s* orbital

$$\Psi^{\text{Pseudo}}(r) \underset{r>r_c}{=} \Psi^{\text{all-Electron}}(r)$$

Justification for pseudopotential formalism



PHYSICAL REVIEW VOLUME 116, NUMBER 2 OCTOBER 15, 1959

New Method for Calculating Wave Functions in Crystals and Molecules*

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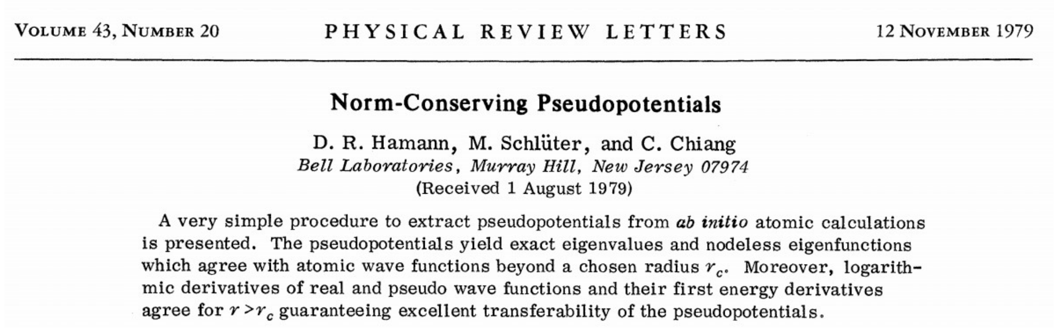
(Received January 5, 1959; revised manuscript received June 1, 1959)

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_α which are best described as the smooth part of symmetrized Bloch functions. The wave equation satisfied by φ_α 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.

Valence electron orthogonality to core electrons provide a repulsive effective potential, resulting in an effective smooth "pseudopotential" for valence electrons.

Norm-conserving pseudopotential construction schemes

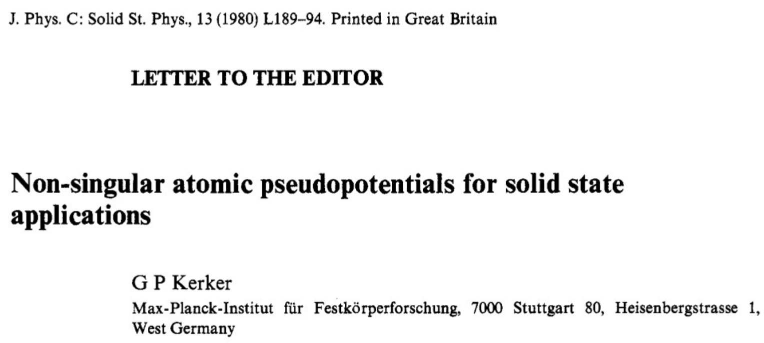


VOLUME 43, NUMBER 20 PHYSICAL REVIEW LETTERS 12 NOVEMBER 1979

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

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Norm-conserving pseudopotentials -- continued

Constructed from all-electron treatments of spherical atoms or ions:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V^{\text{all-Electron}}(r) - \epsilon_{nl}\right)\Psi_{nl}^{\text{all-Electron}}(r) = 0$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V^{\text{Pseudo}}(r) - \epsilon_{nl}\right)\Psi_{nl}^{\text{Pseudo}}(r) = 0$$

Require:

$$V^{\text{Pseudo}}(r) \equiv V^{\text{all-Electron}}(r) \quad \text{for } r > r_c$$

$$\Psi_{nl}^{\text{Pseudo}}(r) \equiv \Psi_{nl}^{\text{all-Electron}}(r) \quad \text{for } r > r_c$$

Also require:

$$\int_{r \le r_c} d^3r \left|\Psi_{nl}^{\text{Pseudo}}(r)\right|^2 \equiv \int_{r \le r_c} d^3r \left|\Psi_{nl}^{\text{all-Electron}}(r)\right|^2$$

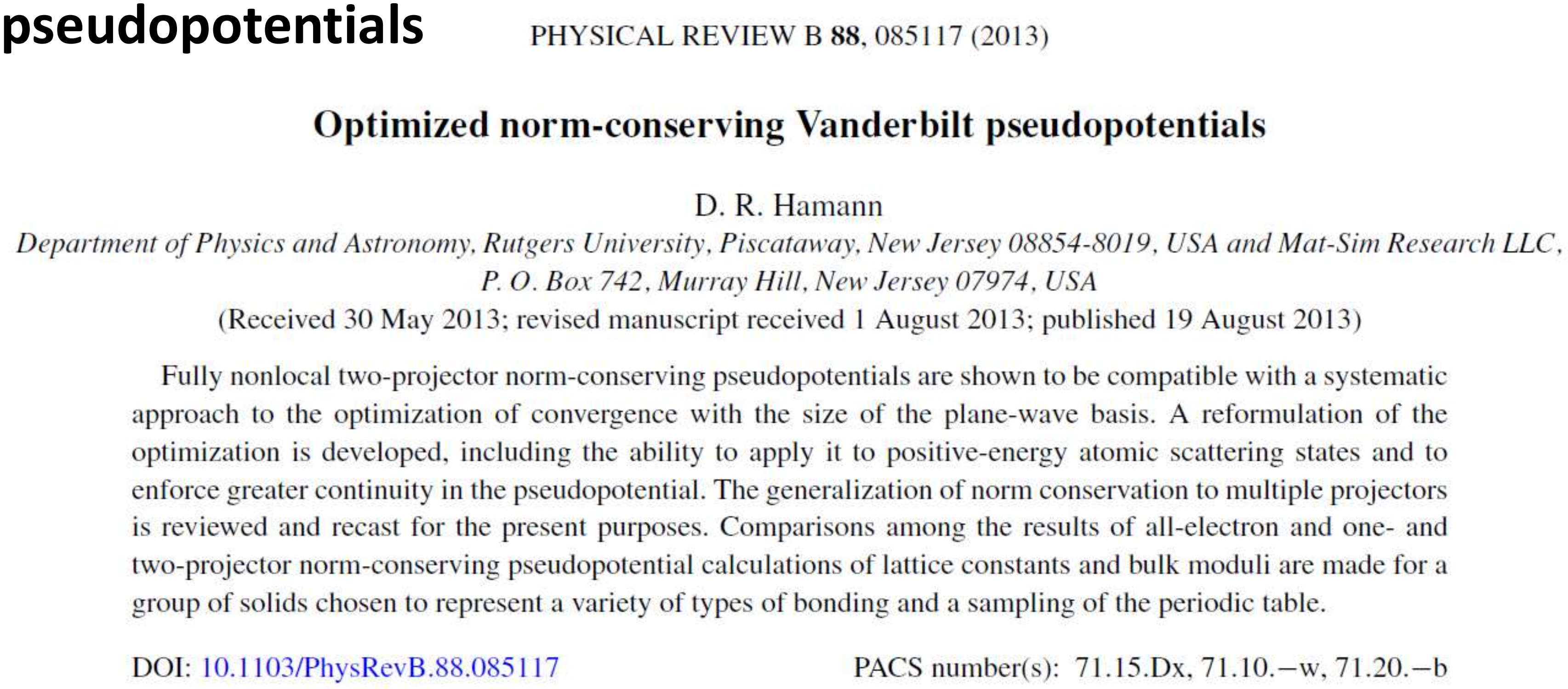
Norm conservation condition; has several benefits

Procedure can be carried out for one orbital Ψ_{nl} at a time

$$V^{\text{Pseudo}}(r) = V_{\text{loc}}^{\text{Pseudo}}(r) + \sum_{nl} V_{nl}^{\text{Pseudo}}(r)\mathscr{P}_{nl}$$

Non-local projector operator

Recent improvements to norm-conserving pseudopotentials



PHYSICAL REVIEW B **88**, 085117 (2013)

Optimized norm-conserving Vanderbilt pseudopotentials

D. R. Hamann
Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854-8019, USA and Mat-Sim Research LLC, P. O. Box 742, Murray Hill, New Jersey 07974, USA

(Received 30 May 2013; revised manuscript received 1 August 2013; published 19 August 2013)

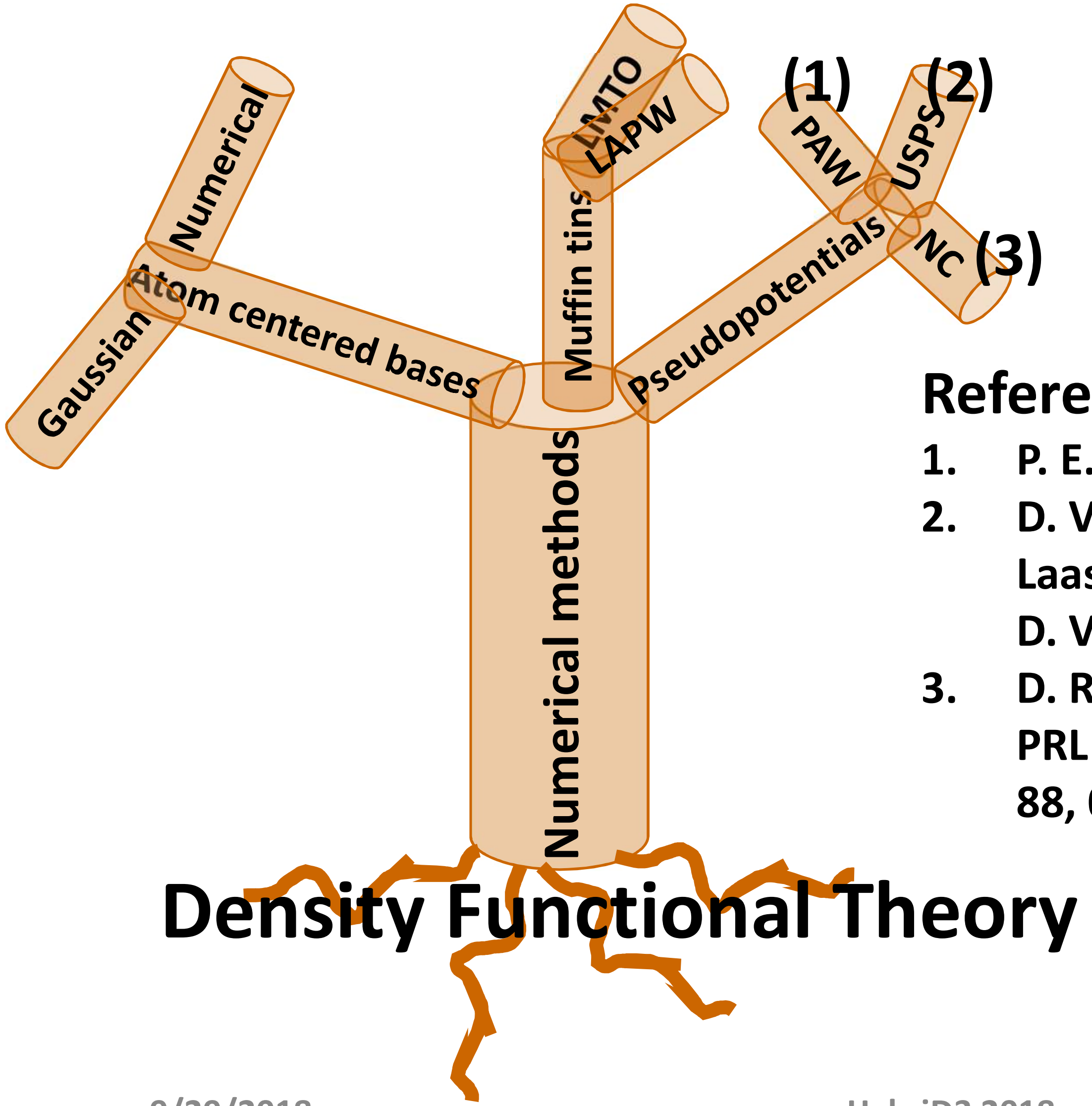
Fully nonlocal two-projector norm-conserving pseudopotentials are shown to be compatible with a systematic approach to the optimization of convergence with the size of the plane-wave basis. A reformulation of the optimization is developed, including the ability to apply it to positive-energy atomic scattering states and to enforce greater continuity in the pseudopotential. The generalization of norm conservation to multiple projectors is reviewed and recast for the present purposes. Comparisons among the results of all-electron and one- and two-projector norm-conserving pseudopotential calculations of lattice constants and bulk moduli are made for a group of solids chosen to represent a variety of types of bonding and a sampling of the periodic table.

DOI: 10.1103/PhysRevB.88.085117 PACS number(s): 71.15.Dx, 71.10.−w, 71.20.−b

➔ **Improves the accuracy of the norm conserving formulation and allows for accurate plane wave representations of the wavefunctions:**

$$\Psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}\ \text{for}\ |\mathbf{k}+\mathbf{G}|\le K_{\max}} \tilde{u}_{\mathbf{k}}(\mathbf{G})\, e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

Other plane wave compatible schemes --



References:

1. P. E. Blöchl, PRB 50, 17953 (1994)
2. D. Vanderbilt, PRB 41, 7892 (1990); K. Laasonen, A. Pasquarello, R. Car, C. Lee, D. Vanderbilt, PRB 47, 10142 (1993)
3. D. R. Hamann, M. Schlüter, C. Chiang, PRL 43, 1494 (1979); D. R. Hamann, PRB 88, 085117 (2013)

Basic ideas of the Projector Augmented Wave (PAW) method

Peter Blöchl,
Institute of Theoretical Physics
TU Clausthal, Germany

Blöch presented his ideas at ES93 --"PAW: an all-electron method for first-principles molecular dynamics"
Reference: P. E. Blöchl, PRB 50, 17953 (1994)

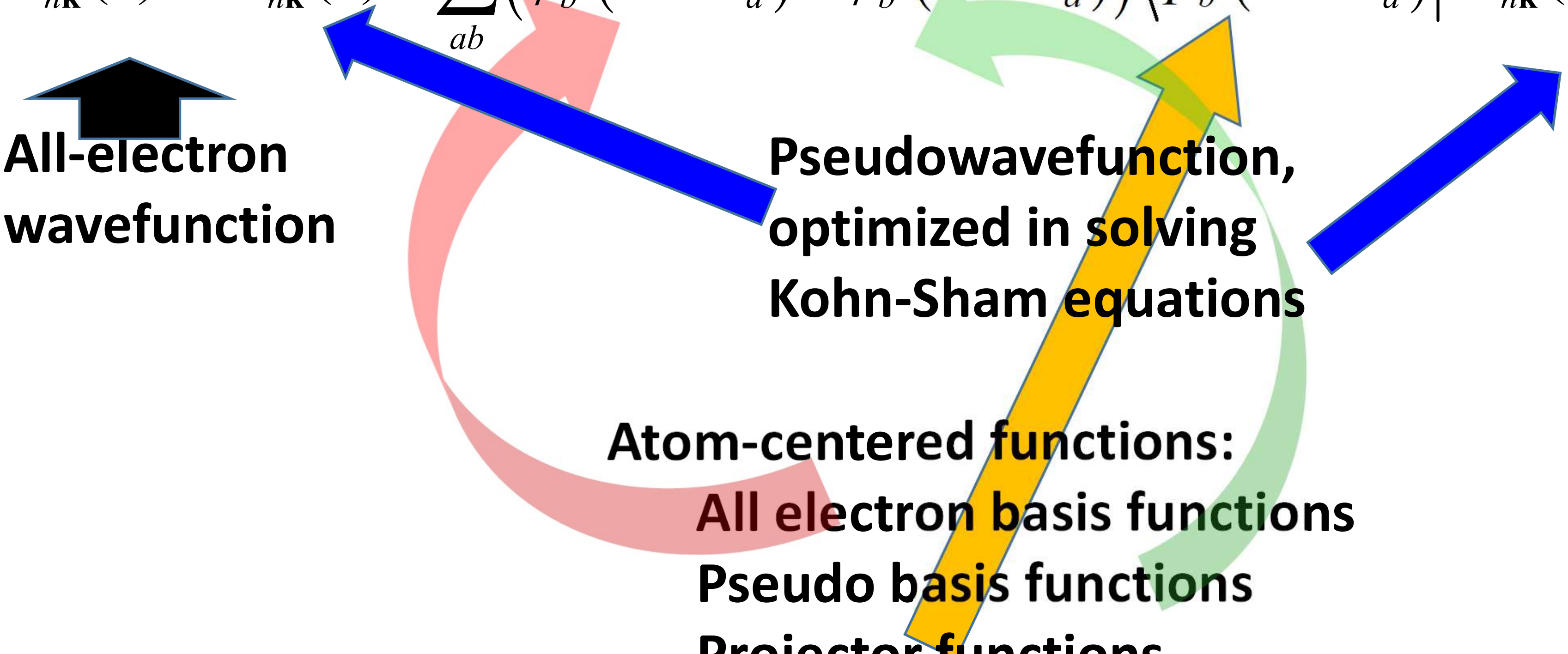
Features

- Operationally similar to other pseudopotential methods, particularly to the ultra-soft pseudopotential method of D. Vanderbilt; often run within frozen core approximation
- Can retrieve approximate "all-electron" wavefunctions from the results of the calculation; useful for NMR analysis for example
- May have additional accuracy controls particularly of the higher multipole Coulombic contributions.

Basic ideas of the Projector Augmented Wave (PAW) method

- **Valence electron wavefunctions are approximated by the form**

$$\Psi_{n\mathbf{k}}(\mathbf{r}) \approx \tilde{\Psi}_{n\mathbf{k}}(\mathbf{r}) + \sum_{ab}\left(\varphi_b^a(\mathbf{r}-\mathbf{R}_a) - \tilde{\varphi}_b^a(\mathbf{r}-\mathbf{R}_a)\right)\left\langle \tilde{p}_b^a(\mathbf{r}-\mathbf{R}_a) \middle| \tilde{\Psi}_{n\mathbf{k}}(\mathbf{r})\right\rangle$$



All-electron wavefunction

Pseudowavefunction, optimized in solving Kohn-Sham equations

Atom-centered functions:

All electron basis functions

Pseudo basis functions

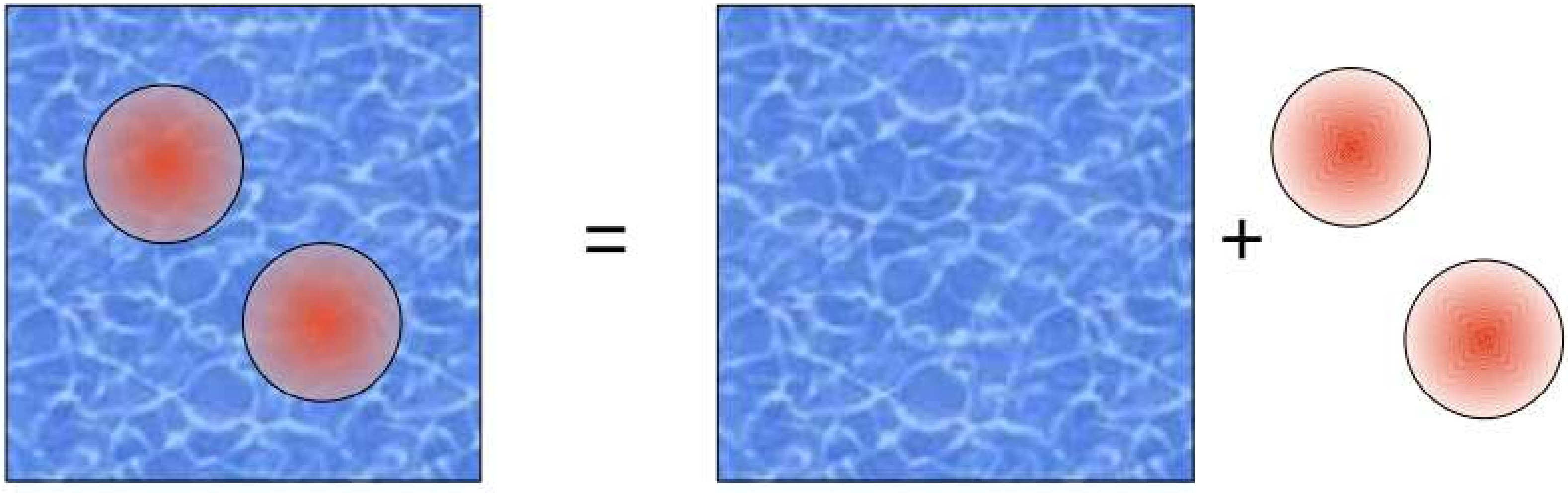
Projector functions

$\left\{\tilde{\Psi}_{n\mathbf{k}}(\mathbf{r})\right\}$: determined self-consistently within calculation

$\left\{\varphi_b^a(\mathbf{r}), \tilde{\varphi}_b^a(\mathbf{r}), \tilde{p}_b^a(\mathbf{r})\right\}$: part of pseudopotential construction; stored in PAW dataset

Basic ideas of the Projector Augmented Wave (PAW) method

- **Evaluation of the total electronic energy:**



$$E_{\text{total}} = \tilde{E}_{\text{total}} + \sum_a \Delta E_a$$

Pseudoenergy (evaluated in plane wave basis or on regular grid)

One-center atomic contributions (evaluated within augmentation spheres)

Comment on one center energy contributions

- **Norm-conserving pseudopotential scheme using the Kleinman-Bylander method (PRL 48, 1425 (1982)):**

  The non-local pseudopotential contributions for site a:

  $$\Delta E_a = \sum_{n\mathbf{k},b} W_{n\mathbf{k}} \left\langle \tilde{\Psi}_{n\mathbf{k}} \middle| \tilde{\chi}^a_b \right\rangle \left\langle \tilde{\chi}^a_b \middle| \tilde{\Psi}_{n\mathbf{k}} \right\rangle, \text{where } \tilde{\chi}^a_b(\mathbf{r}-\mathbf{R}^a) \text{ are}$$

  fixed functions depending on the non-local pseudopotentials and corresponding pseudobasis functions; $W_{n\mathbf{k}}$ are occupancy and sampling weights.

- **PAW and USPS :**

  $$\Delta E_a = \sum_{n\mathbf{k},bb'} W_{n\mathbf{k}} \left\langle \tilde{\Psi}_{n\mathbf{k}} \middle| \tilde{p}^a_b \right\rangle M^a_{bb'} \left\langle \tilde{p}^a_{b'} \middle| \tilde{\Psi}_{n\mathbf{k}} \right\rangle, \text{where } \tilde{p}^a_b(\mathbf{r}-\mathbf{R}^a) \text{ are}$$

  projector functions, $M^a_{bb'}$ are matrix elements depending on all-electron and pseudobasis functions, and $W_{n\mathbf{k}}$ are occupancy and Brillouin zone sampling weights.

Comment on one center energy contributions -- continued for PAW and USPS

$M^a_{bb'}$ matrix elements (different for USPS and PAW) are evaluated within the augmentation spheres. For example, the kinetic energy term:

$$K^a_{bb'} = \delta_{l_b l_{b'}} \delta_{m_b m_{b'}} \frac{\hbar^2}{2m} \left(\int_0^{r_c} dr \left(\frac{d\phi^a_b(r)}{dr} \frac{d\phi^a_{b'}(r)}{dr} - \frac{d\tilde{\phi}^a_b(r)}{dr} \frac{d\tilde{\phi}^a_{b'}(r)}{dr} \right) \right.$$

$$\left. + l_b(l_b+1) \left(\int_0^{r_c} \frac{dr}{r^2} \left(\phi^a_b(r)\phi^a_{b'}(r) - \tilde{\phi}^a_b(r)\tilde{\phi}^a_{b'}(r) \right) \right) \right)$$

where $\varphi^a_b(\mathbf{r}) \equiv \dfrac{\phi^a_b(r)}{r} Y_{l_b m_b}(\hat{\mathbf{r}})$ and $\tilde{\varphi}^a_b(\mathbf{r}) \equiv \dfrac{\tilde{\phi}^a_b(r)}{r} Y_{l_b m_b}(\hat{\mathbf{r}})$

Note that for USPS, the operator $Q^a_{bb'}(r) \equiv \left(\phi^a_b(r)\phi^a_{b'}(r) - \tilde{\phi}^a_b(r)\tilde{\phi}^a_{b'}(r) \right)$ is pseudized, while for PAW it is evaluated within matrix elements and "compensation charges" are added. In both cases, multipole moments are conserved.

Summary of properties of norm-conserving (NC), ultra-soft-pseudopotential (USPS) and projector augmented wave (PAW) methods

	NC	USPS	PAW
Conservation of charge	✓	✓	✓
Multipole moments in Hartree interaction		✓	✓
Retrieve all-electron wavefunction			✓

Some details – use of "compensation charge"

PAW approximation to valence all-electron wave function

$$\Psi_{n\mathbf{k}}(\mathbf{r}) \approx \tilde{\Psi}_{n\mathbf{k}}(\mathbf{r}) + \sum_{ab}\left(\varphi_b^a(\mathbf{r}-\mathbf{R}_a) - \tilde{\varphi}_b^a(\mathbf{r}-\mathbf{R}_a)\right)\left\langle \tilde{p}_b^a(\mathbf{r}-\mathbf{R}_a) \middle| \tilde{\Psi}_{n\mathbf{k}}(\mathbf{r})\right\rangle$$

PAW approximation to all-electron density

$$n_{\text{valence}}(\mathbf{r}) \approx \sum_{n\mathbf{k}} W_{n\mathbf{k}} \left|\Psi_{n\mathbf{k}}(\mathbf{r})\right|^2$$

$$\approx \sum_{n\mathbf{k}} W_{n\mathbf{k}} \left|\tilde{\Psi}_{n\mathbf{k}}(\mathbf{r})\right|^2$$

$$+\sum_{n\mathbf{k}} W_{n\mathbf{k}} \sum_{a,bb'} \left\langle \tilde{\Psi}_{n\mathbf{k}} \middle| \tilde{p}_b^a \right\rangle \left\langle \tilde{p}_{b'}^a \middle| \tilde{\Psi}_{n\mathbf{k}} \right\rangle \left(\varphi_b^a(\mathbf{r}-\mathbf{R}_a)\varphi_{b'}^a(\mathbf{r}-\mathbf{R}_a) - \tilde{\varphi}_b^a(\mathbf{r}-\mathbf{R}_a)\tilde{\varphi}_{b'}^a(\mathbf{r}-\mathbf{R}_a)\right)$$

$$\equiv \sum_{n\mathbf{k}} W_{n\mathbf{k}} \left(\left|\tilde{\Psi}_{n\mathbf{k}}(\mathbf{r})\right|^2 + \sum_{a,bb'} \left\langle \tilde{\Psi}_{n\mathbf{k}} \middle| \tilde{p}_b^a \right\rangle \left\langle \tilde{p}_{b'}^a \middle| \tilde{\Psi}_{n\mathbf{k}} \right\rangle Q_{bb'}^a(\mathbf{r}-\mathbf{R}_a) \right)$$

$$\equiv \tilde{n}(\mathbf{r}) + \sum_a \left(n^a(\mathbf{r}-\mathbf{R}_a) - \tilde{n}^a(\mathbf{r}-\mathbf{R}_a) \right)$$

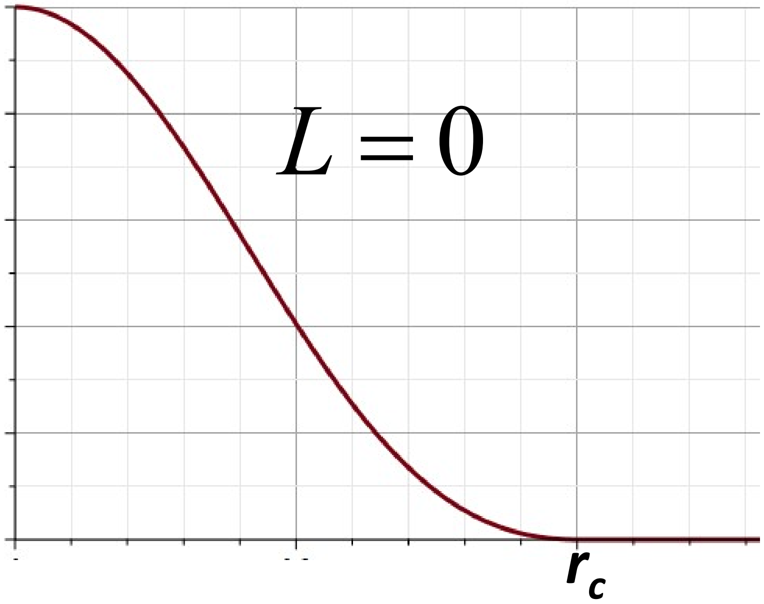
$$= \tilde{n}(\mathbf{r}) + \sum_a \hat{n}^a(\mathbf{r}-\mathbf{R}^a) + \sum_a \left(n^a(\mathbf{r}-\mathbf{R}_a) - \tilde{n}^a(\mathbf{r}-\mathbf{R}_a) - \hat{n}^a(\mathbf{r}-\mathbf{R}^a) \right)$$

Some details – use of “compensation charge” -- continued

Compensation charge is designed to have the same multipole moments of one-center charge differences:

$$\int_{r \le r_c^a} d^3r\ r^L Y_{LM}(\hat{\mathbf{r}})\hat{n}^a(\mathbf{r}) = \int_{r \le r_c^a} d^3r\ r^L Y_{LM}(\hat{\mathbf{r}})\left(n^a(\mathbf{r}) - \tilde{n}^a(\mathbf{r})\right)$$

Typical shape of compensation charge for L=0 component --



Some details – use of "compensation charge" -- continued

The inclusion of the "compensation" charge ensures

1. Hartree energy of smooth charge density represents correct charge
2. Hartree energy contributions of one-center charge is confined within augmentation sphere:

$$\int_{r\le r_c^a} d^3r' \frac{n^a(\mathbf{r})-\tilde{n}^a(\mathbf{r})-\hat{n}^a(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} = \begin{cases} V^a_{\text{Hartree}}(\mathbf{r}) & \text{for } r\le r_c^a \\ 0 & \text{for } r > r_c^a \end{cases}$$

Some details – form of exchange-correlation contributions

non-linear core correction (S. G. Louie et al. PRB 26, 1738 (1982))

For $E_{xc}[n(\mathbf{r})] \equiv \int d^3r\, K_{xc}(n(\mathbf{r})):$

Smooth contribution: $\tilde{E}_{xc} = E_{xc}[\tilde{n}(\mathbf{r}) + \tilde{n}_{\text{core}}(\mathbf{r})]$

One-center contributions: $E^a_{xc} - \tilde{E}^a_{xc} = E_{xc}[n^a(\mathbf{r}) + n^a{}_{\text{core}}(\mathbf{r})] - E_{xc}[\tilde{n}^a(\mathbf{r}) + \tilde{n}^a_{\text{core}}(\mathbf{r})]$

Note that VASP and Quantum-Espresso use

$\tilde{E}_{xc}[\tilde{n}(\mathbf{r}) + \tilde{n}_{\text{core}}(\mathbf{r}) + \hat{n}(\mathbf{r})]$

and $\tilde{E}_{xc}[\tilde{n}^a(\mathbf{r}) + \tilde{n}^a_{\text{core}}(\mathbf{r}) + \hat{n}^a(\mathbf{r})]$

which can cause trouble occasionally.

Pseudopotential schemes enable the accurate use of plane wave and regular grid based numerical methods

Convergence of plane wave expansions:

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{u}_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \qquad \left(|\mathbf{k}+\mathbf{G}| < K_{\max}\right)$$

Electron density: $n(\mathbf{r}) = \sum_{n\mathbf{k}\ (\mathrm{occ})} w_{n\mathbf{k}} \left|\Psi_{n\mathbf{k}}(\mathbf{r})\right|^2$

$$n(\mathbf{r}) = \sum_{n\mathbf{k}\ (\mathrm{occ})} w_{n\mathbf{k}} \left|\sum_{\mathbf{G}} \tilde{u}_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}\right|^2 = \sum_{\mathbf{G}} \tilde{n}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

$$|\mathbf{k}+\mathbf{G}| \le K_{\max} \qquad\qquad |\mathbf{G}| \le 2K_{\max}$$

Some convenient numerical "tricks" involved with Fourier transforms using discrete Fourier transforms

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\substack{\mathbf{G} \\ (|\mathbf{k}+\mathbf{G}| \leq K_{\max})}} \tilde{u}_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

⇐Discrete summation due to lattice periodicity

Discrete Fourier transforms ➔ Fast Fourier transforms

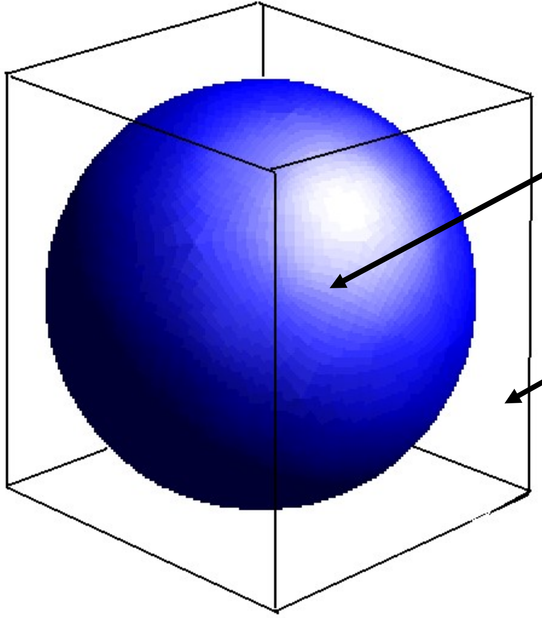
FFT equations http://www.fftw.org/

$$f(n_1, n_2, n_3) = \sum_{m_1, m_2, m_3} \tilde{f}(m_1, m_2, m_3) e^{i2\pi\left(\frac{n_1 m_1}{N_1} + \frac{n_2 m_2}{N_2} + \frac{n_3 m_3}{N_3}\right)}$$

$$\tilde{f}(m_1, m_2, m_3) = \frac{1}{N_1 N_2 N_3} \sum_{n_1, n_2, n_3} f(n_1, n_2, n_3) e^{-i2\pi\left(\frac{n_1 m_1}{N_1} + \frac{n_2 m_2}{N_2} + \frac{n_3 m_3}{N_3}\right)}$$

Reciprocal space

FFT grid size

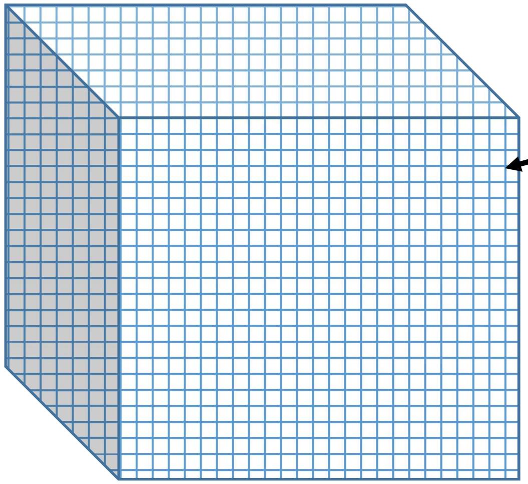


$$|\mathbf{G}| \le K_{max}$$

Enclosing parallelepiped

$$\mathbf{G} = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3$$

$$0 \le n_i \le N_i$$



Real space grid points

$$\mathbf{r} = \frac{m_1}{N_1}\mathbf{a}_1 + \frac{m_2}{N_2}\mathbf{a}_2 + \frac{m_3}{N_3}\mathbf{a}_3$$

$$\mathbf{G}\cdot\mathbf{r} = 2\pi\left(\frac{n_1 m_1}{N_1} + \frac{n_2 m_2}{N_2} + \frac{n_3 m_3}{N_3}\right)$$

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  - Projector augmented wave formalism
- **Assessment of the calculations**

Assessment of the calculations

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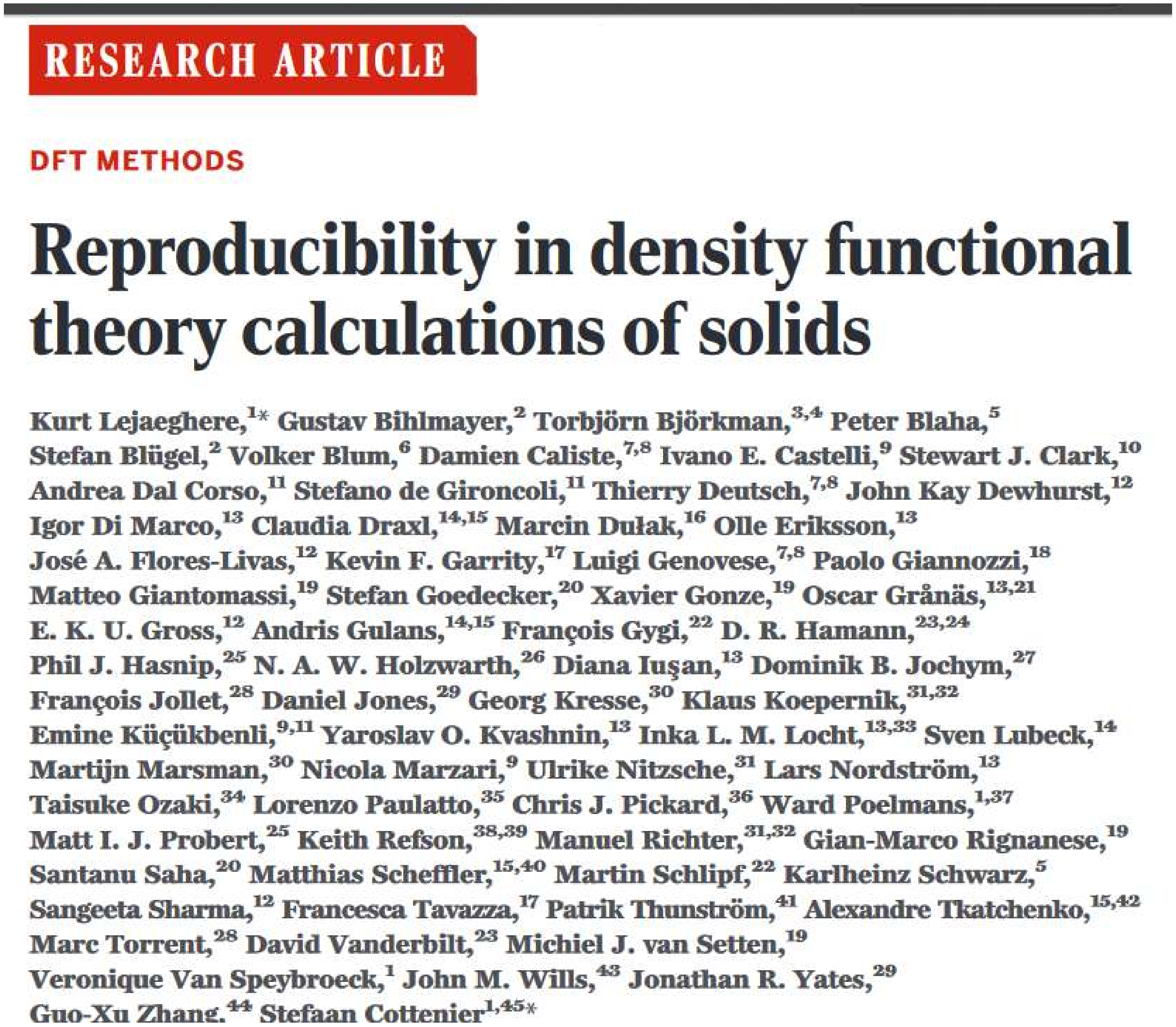
http://science.sciencemag.org/content/sci/351/6280/aad3000.full.pdf



RESEARCH ARTICLE

DFT METHODS

Reproducibility in density functional theory calculations of solids

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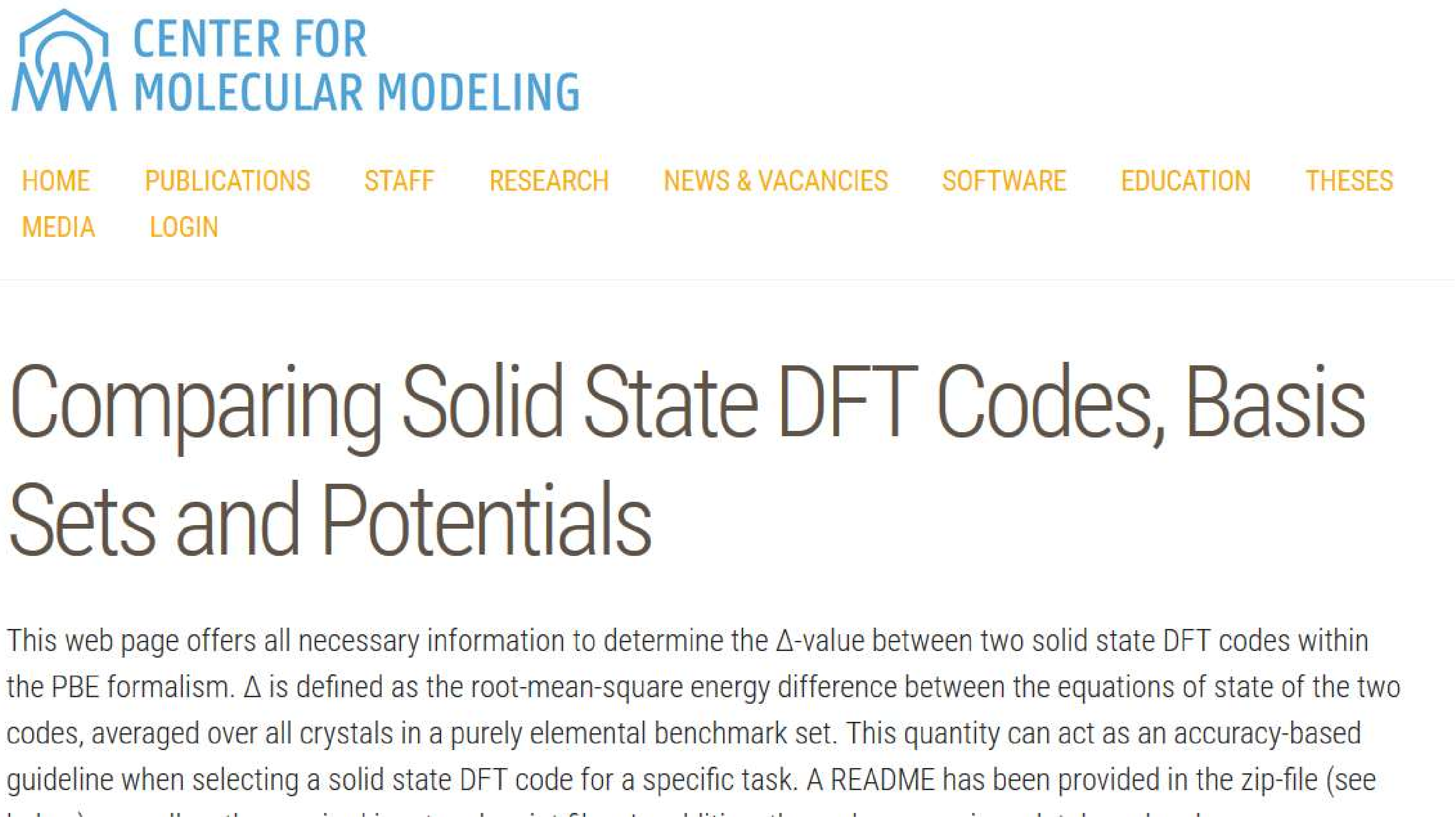
Webpage for standardized comparison of codes

https://molmod.ugent.be/deltacodesdft



Comparing Solid State DFT Codes, Basis Sets and Potentials

This web page offers all necessary information to determine the Δ-value between two solid state DFT codes within the PBE formalism. Δ is defined as the root-mean-square energy difference between the equations of state of the two codes, averaged over all crystals in a purely elemental benchmark set. This quantity can act as an accuracy-based guideline when selecting a solid state DFT code for a specific task. A README has been provided in the zip-file (see

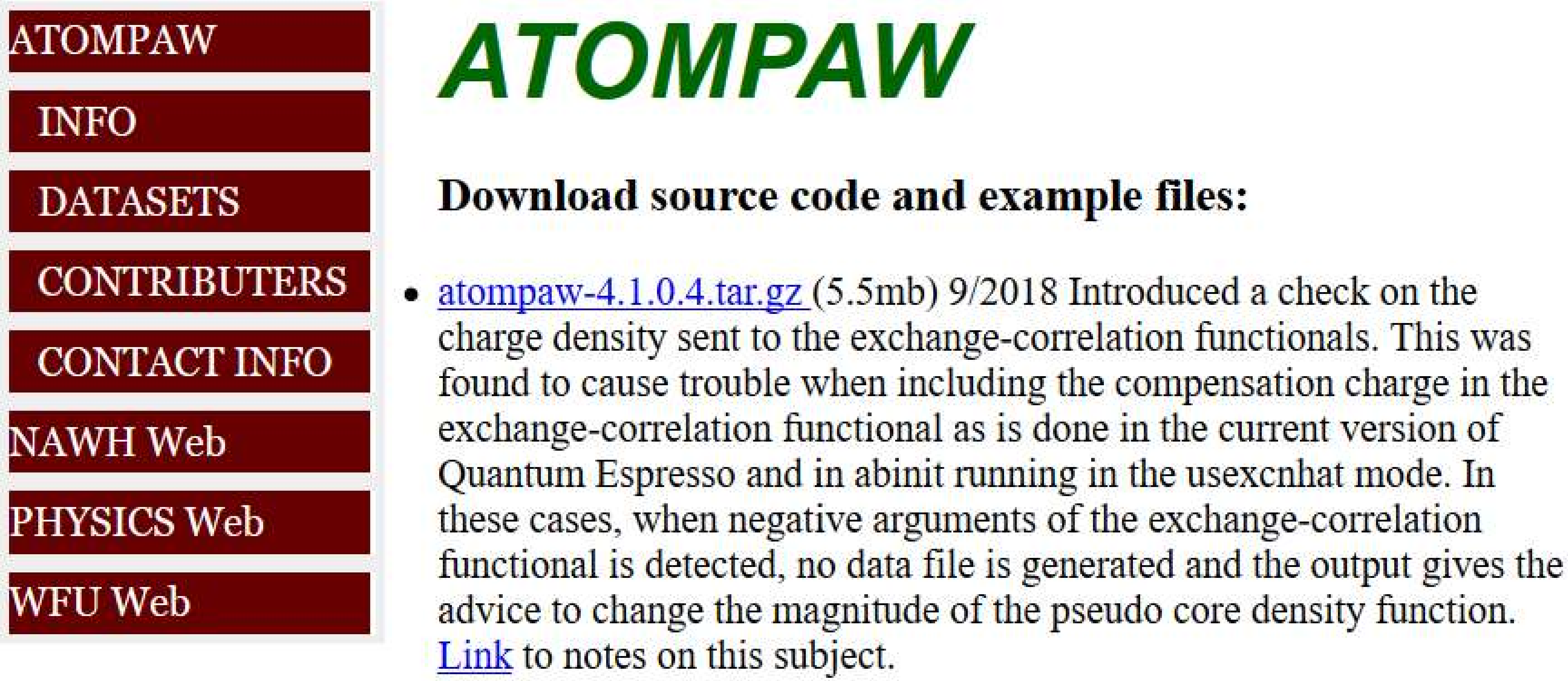
Assessment of your specific calculations

- You can expect that even well-converged calculations will differ between pseudopotential datasets and code packages. It is incumbent on us to trace and document these differences.
- There is some error cancelation in a set of calculations using a given set of pseudopotential datasets and a single code package.
- On the other hand, the best way to validate your results, is to compare two or more independent calculations for a representative sample.

Various code packages

Code for generating PAW datasets

http://pwpaw.wfu.edu



ATOMPAW

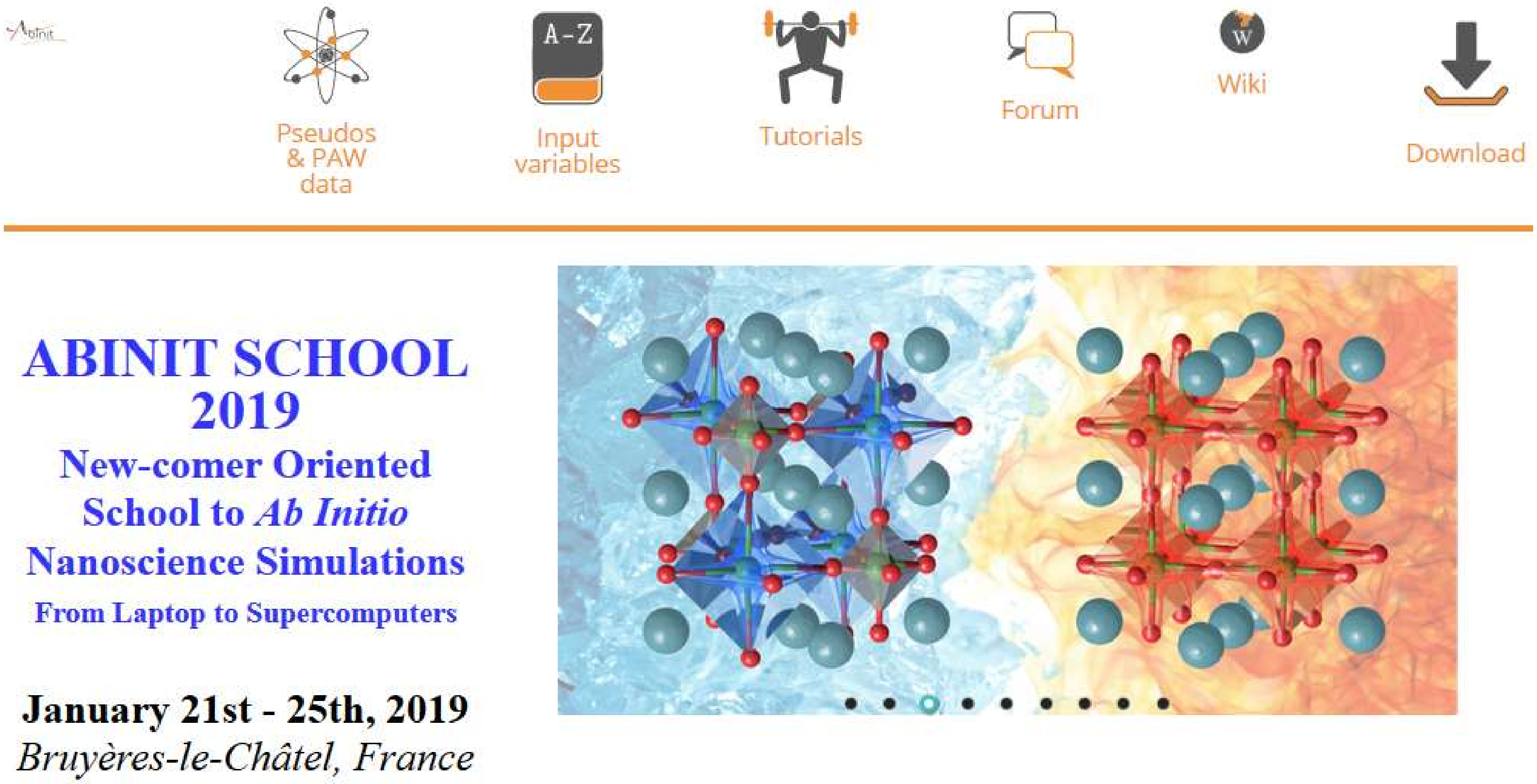
Download source code and example files:

- atompaw-4.1.0.4.tar.gz (5.5mb) 9/2018 Introduced a check on the charge density sent to the exchange-correlation functionals. This was found to cause trouble when including the compensation charge in the exchange-correlation functional as is done in the current version of Quantum Espresso and in abinit running in the usexcnhat mode. In these cases, when negative arguments of the exchange-correlation functional is detected, no data file is generated and the output gives the advice to change the magnitude of the pseudo core density function. Link to notes on this subject.

Various code packages

ABINIT -- Electron structure code package mainly based on plane waves

https://www.abinit.org/



ABINIT SCHOOL 2019

New-comer Oriented School to *Ab Initio* Nanoscience Simulations

From Laptop to Supercomputers

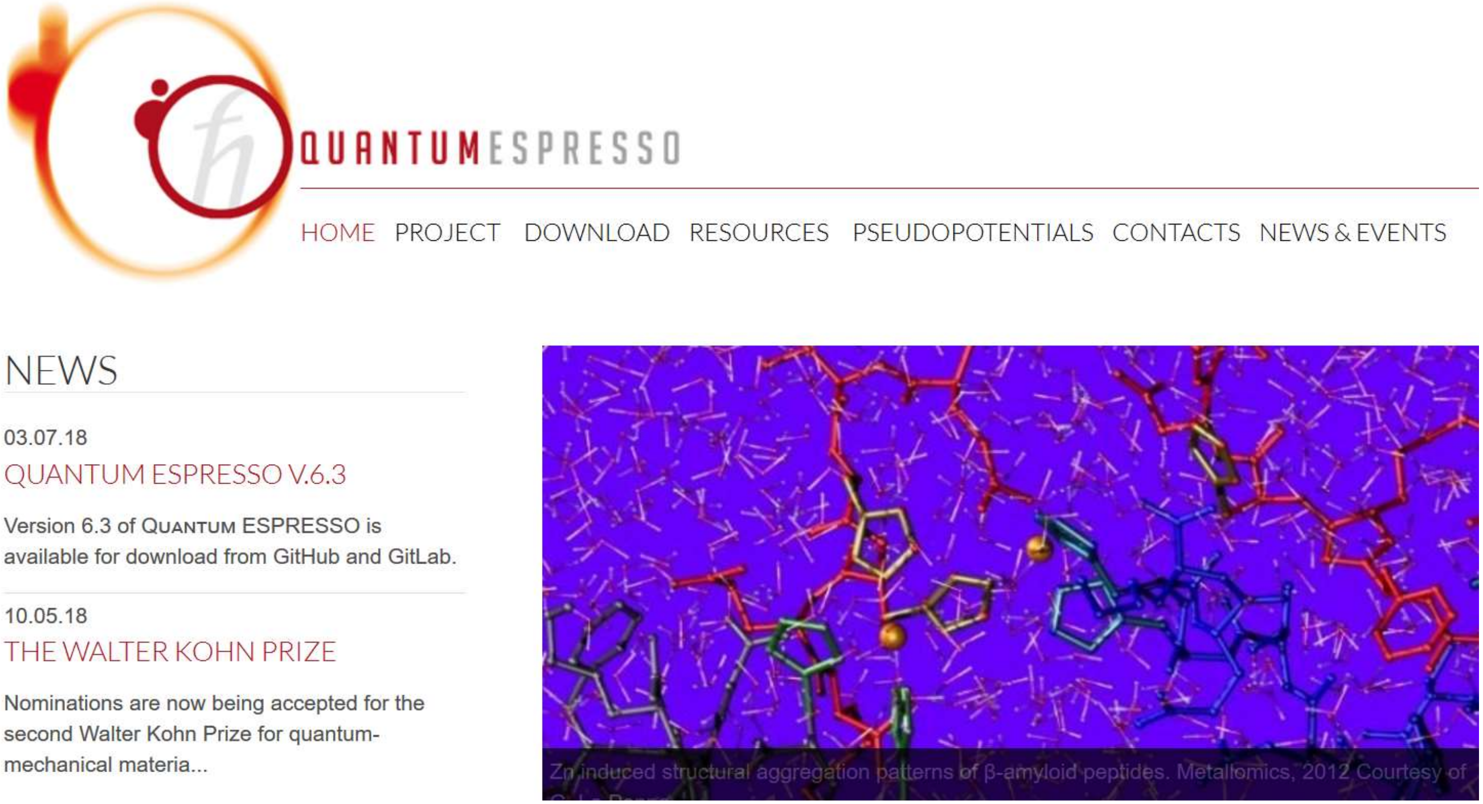
January 21st - 25th, 2019

Bruyères-le-Châtel, France

Various code packages

Quantum Espresso – Electron structure code package mainly based on plane waves

http://www.quantum-espresso.org/



NEWS

03.07.18

QUANTUM ESPRESSO V.6.3

Version 6.3 of QUANTUM ESPRESSO is available for download from GitHub and GitLab.

10.05.18

THE WALTER KOHN PRIZE

Nominations are now being accepted for the second Walter Kohn Prize for quantum-mechanical materia...

Zn induced structural aggregation patterns of β-amyloid peptides. Metallomics, 2012 Courtesy of

General advice about generating PAW datasets

- ATOMPAW code* available at http://pwpaw.wfu.edu
- Develop and test atomic datasets for the full scope of your project ➔ determine r_c^a, define frozen core
- Determine local pseudopotential from self-consistent all-electron potential
- Determine basis functions for valence (and perhaps semicore) states; usually 2 sets of basis functions and projectors for each *l* channel.
- Test binding energy curves for a few binary compounds related to your project.
- Check plane wave (or grid spacing) convergence of your data sets before starting production runs.

*With major modification by Marc Torrent and other Abinit developers.

Recipes for constructing projector and basis functions

$$\varphi_b^a(\mathbf{r}) = \frac{\varphi_b^a(r)}{r} Y_{l_b m_b}(\hat{\mathbf{r}}) \qquad \tilde{\varphi}_b^a(\mathbf{r}) = \frac{\tilde{\varphi}_b^a(r)}{r} Y_{l_b m_b}(\hat{\mathbf{r}}) \qquad \tilde{p}_b^a(\mathbf{r}) = \frac{\tilde{p}_b^a(r)}{r} Y_{l_b m_b}(\hat{\mathbf{r}})$$

Constraints: $\tilde{\varphi}_b^a(r) = \varphi_b^a(r)$ for $r \geq r_c^a$

$\tilde{p}_b^a(r) = 0$ for $r \geq r_c^a$

$\left\langle \tilde{p}_b^a \middle| \tilde{\varphi}_{b'}^a \right\rangle = \delta_{bb'}$

Peter Blöchl's scheme (set #1)

Choose projectors $\tilde{p}_b^a(r)$*

$\Rightarrow$ Derive $\tilde{\varphi}_b^a(r)$

***Typically Bessel-like function with zero value and derivative at r_c^a**

David Vanderbilt's scheme (set #2)

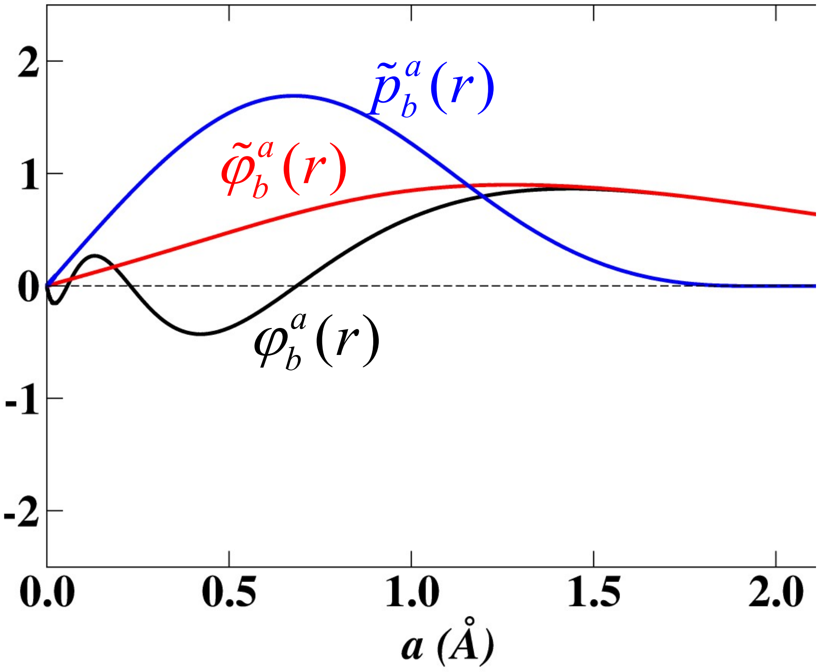
Choose pseudo bases $\tilde{\varphi}_b^a(r)$*

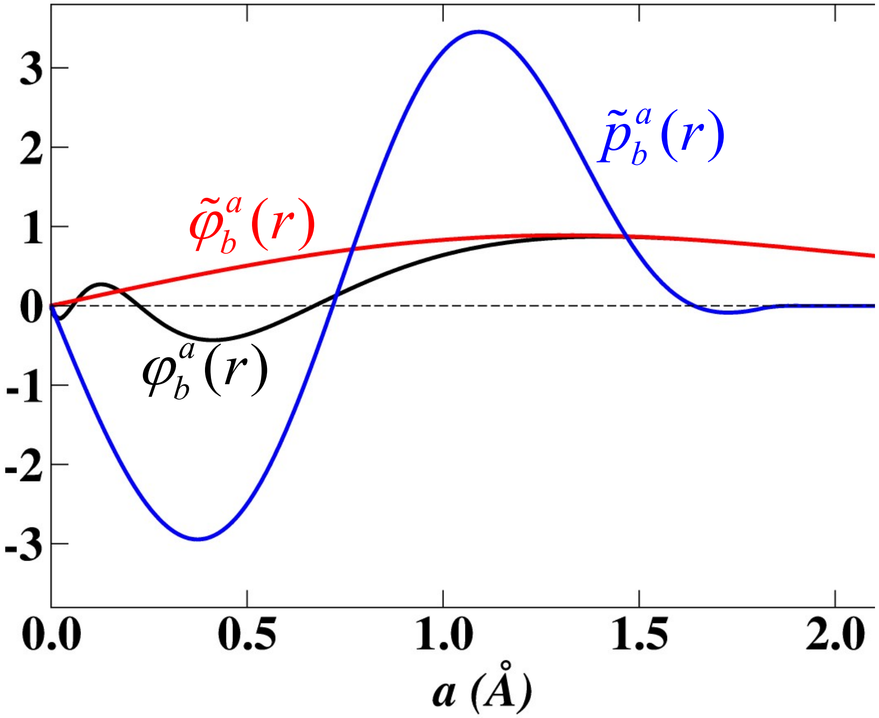
$\Rightarrow$ Derive $\tilde{p}_b^a(r)$

***Polynomial or Bessel function form following RRKJ, PRB 41, 1227 (1990)**

Example projector and basis functions

Br *4s* orbital

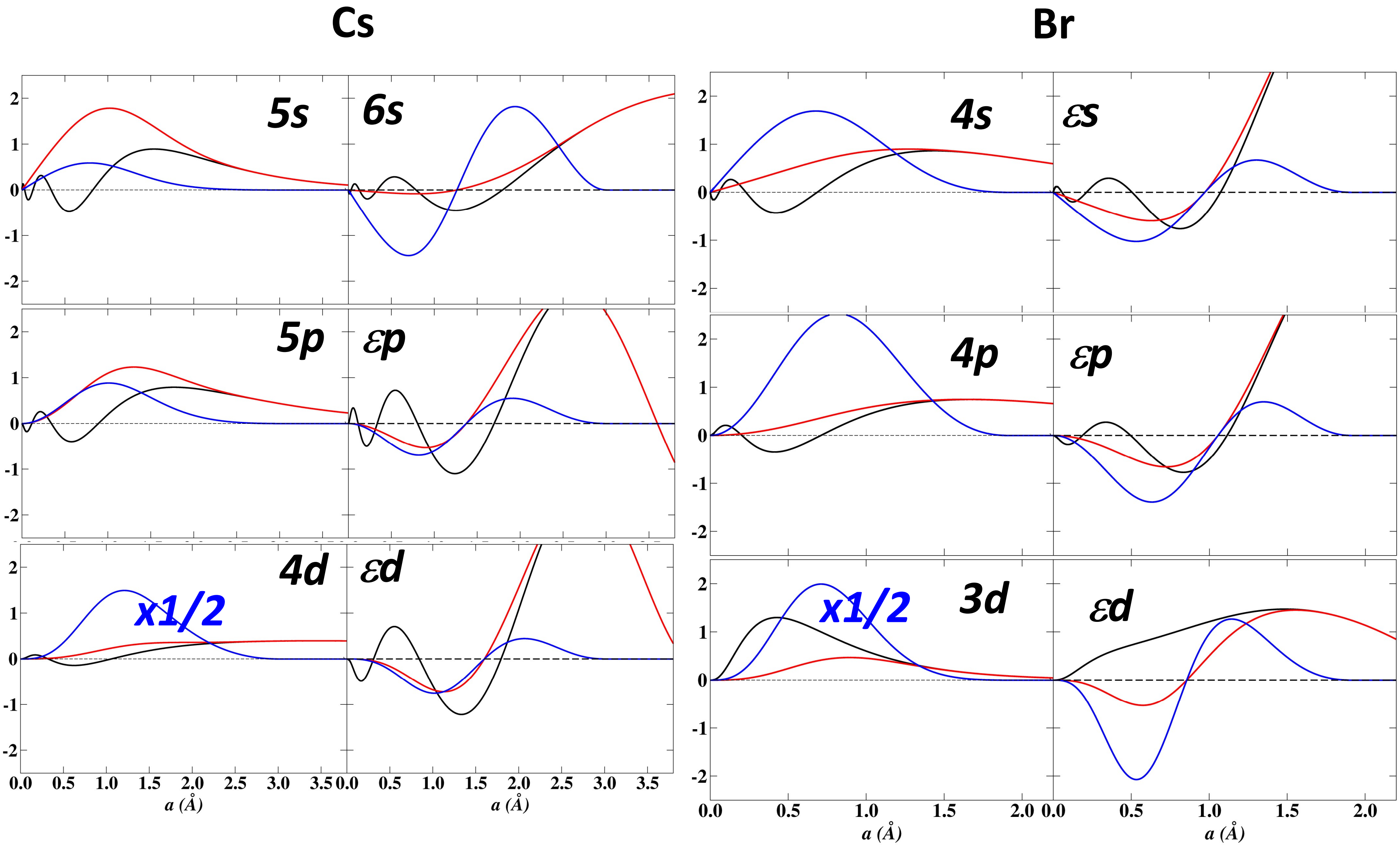




From set #1

From set #2

Set of basis and projector functions for set #1

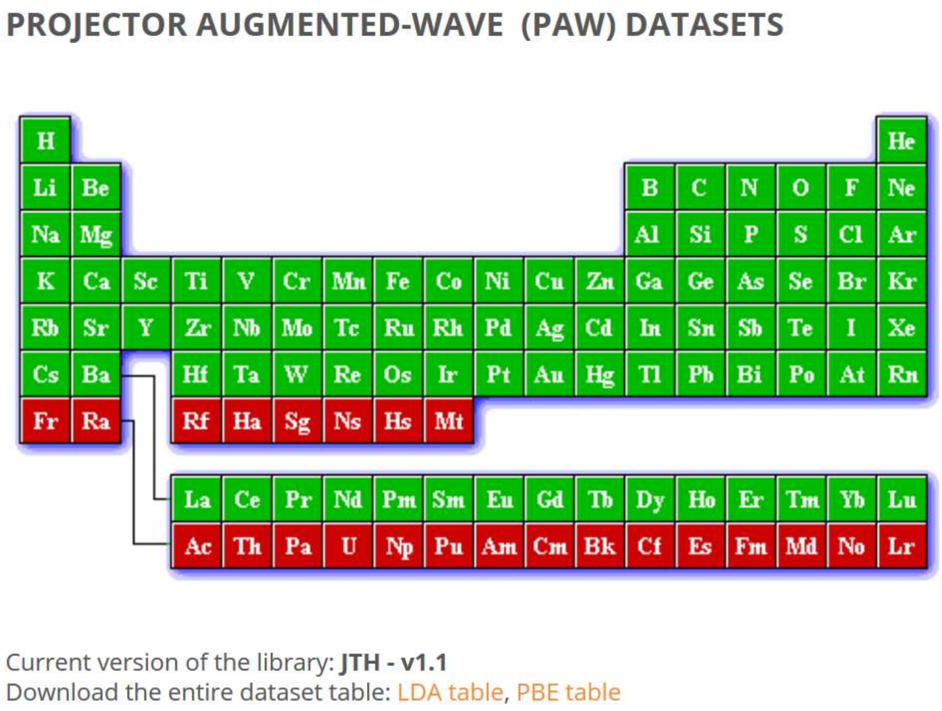

Cs

Br

Sources of pseudopotential and paw datasets on the web

https://www.abinit.org/psp-tables

http://www.quantum-espresso.org/pseudopotentials

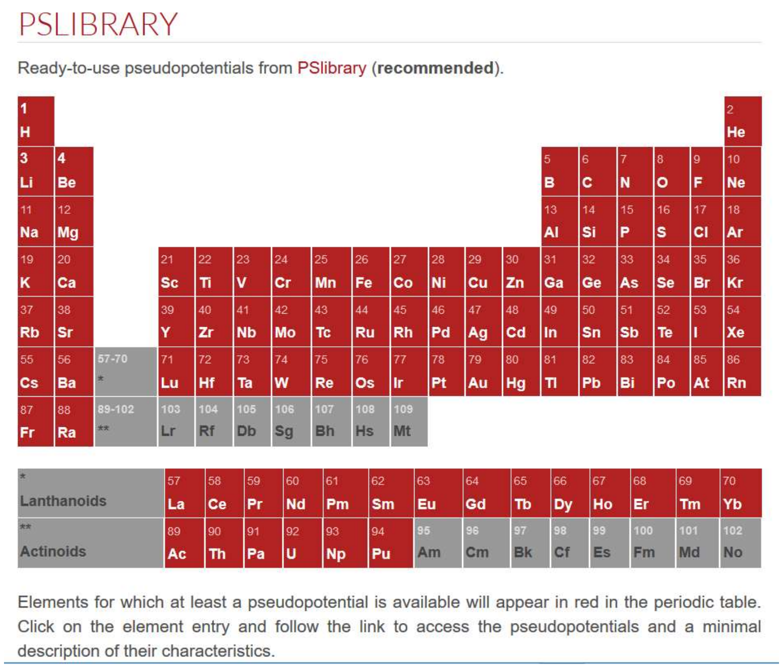


PROJECTOR AUGMENTED-WAVE (PAW) DATASETS

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra		Rf	Ha	Sg	Ns	Hs	Mt									

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Current version of the library: **JTH - v1.1**
Download the entire dataset table: LDA table, PBE table



PSLIBRARY

Ready-to-use pseudopotentials from PSlibrary (**recommended**).

1 H																		2 He
3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-70 *	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-102 **	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt									

* Lanthanoids	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
** Actinoids	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

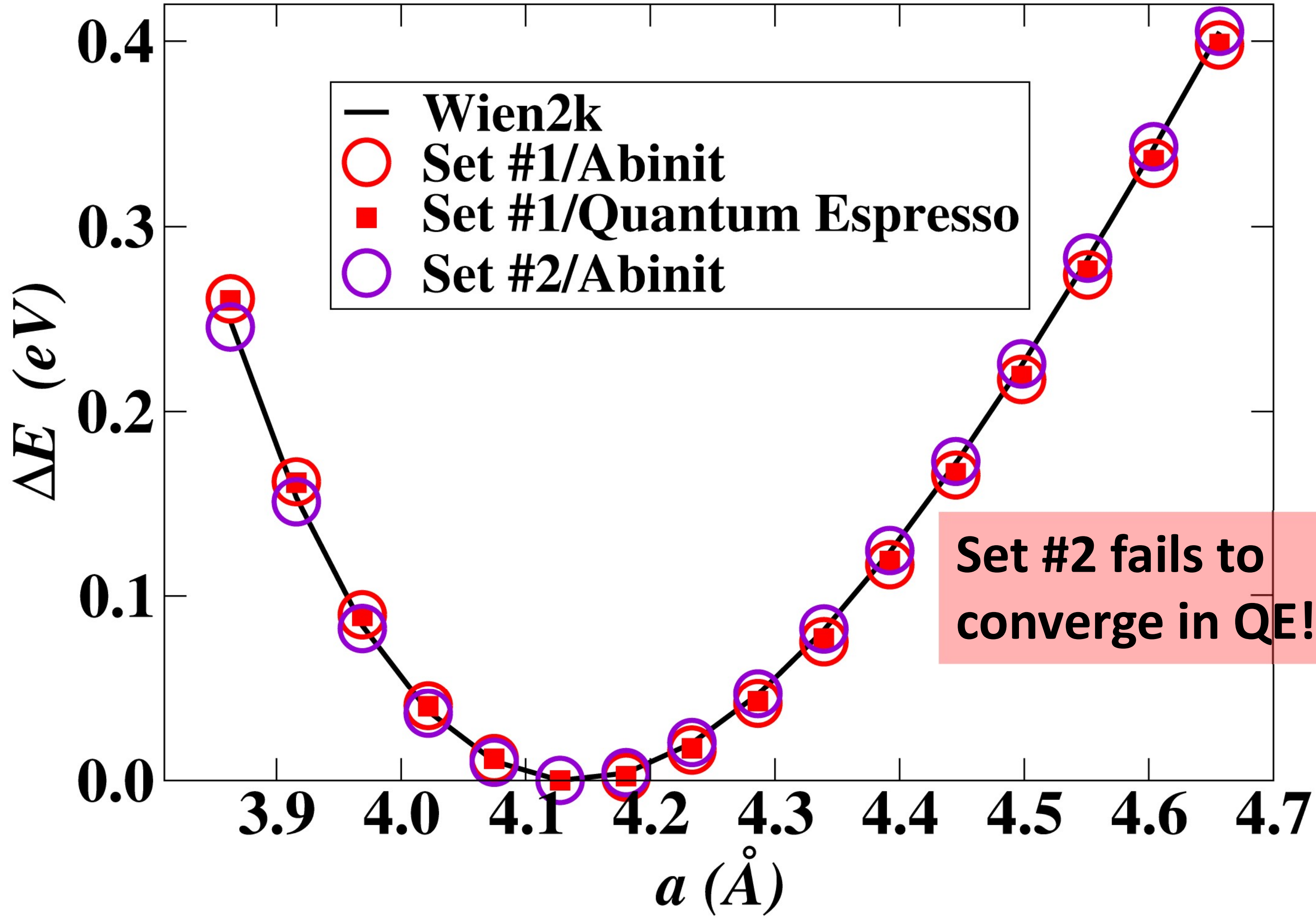
Elements for which at least a pseudopotential is available will appear in red in the periodic table. Click on the element entry and follow the link to access the pseudopotentials and a minimal description of their characteristics.

If you use datasets from the web, it is still your responsibility to test them for accuracy wrt to your project.

Measure of accuracy

Sometimes, calculations can surprise!!

Binding energy curve for CsBr

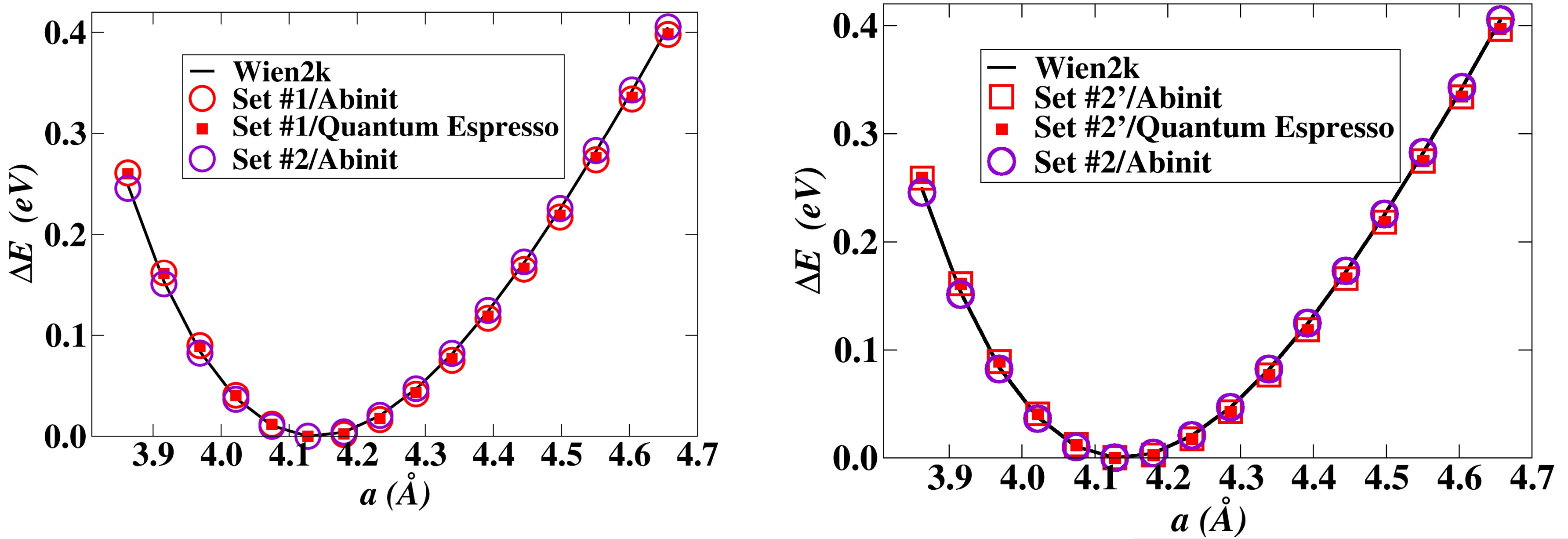


Set #2 fails to converge in QE!

Mystery –

Why does the Cs dataset #1 do well in abinit but fail in espresso??

Binding energy curves for CsBr



Set #2' now converges in QE and abinit!

Answer --

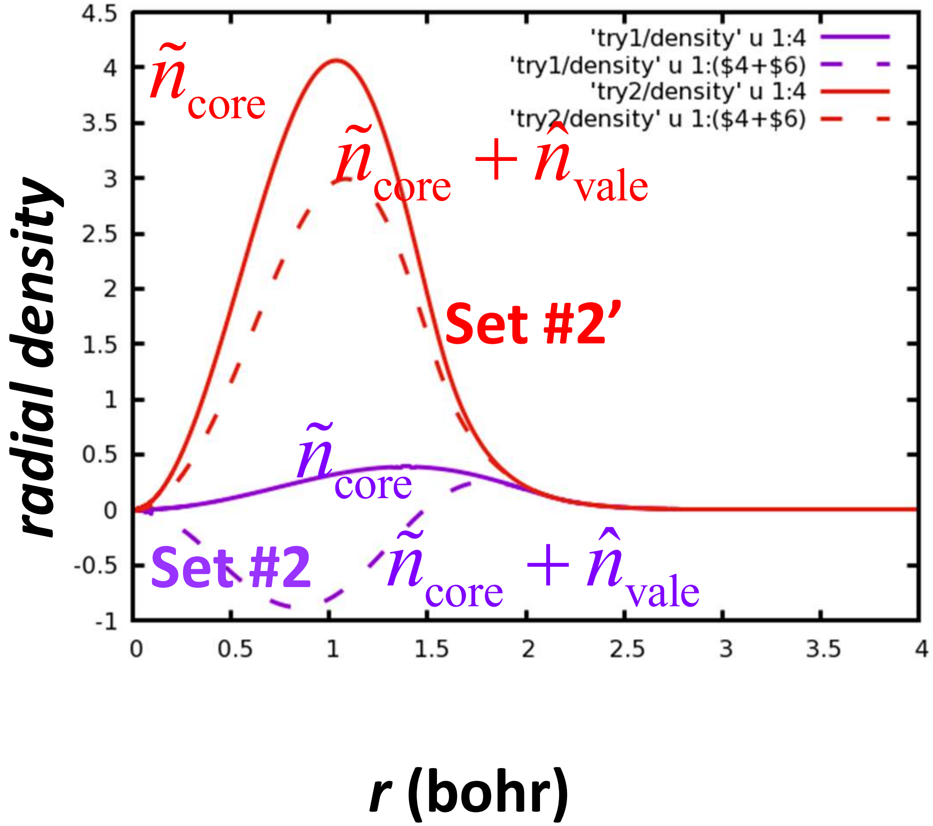
Treatments of the exchange-correlation energies

$$\text{Abinit}: \tilde{E}_{xc} = E_{xc}[\tilde{n}(\mathbf{r}) + \tilde{n}_{\text{core}}(\mathbf{r})]$$

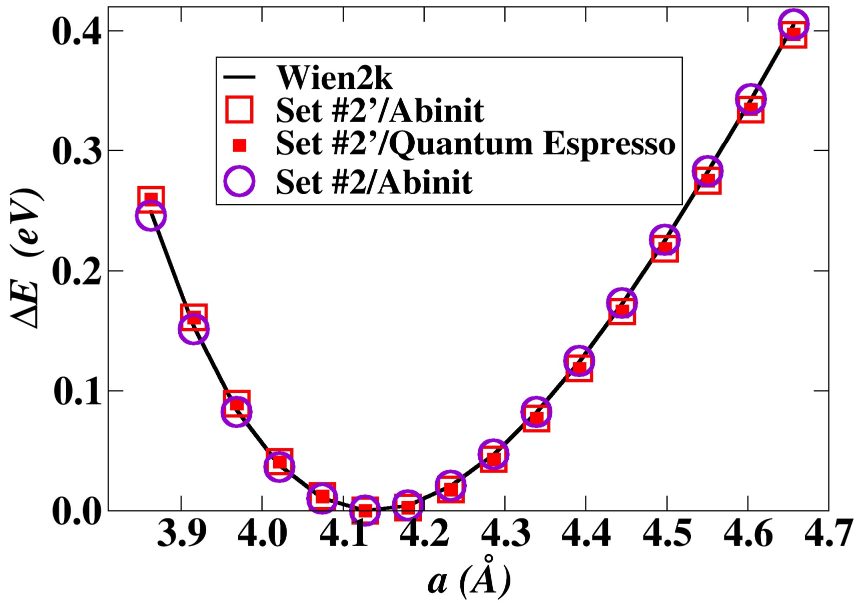
$$\text{QE \& VASP:} \quad \tilde{E}_{xc} = E_{xc}[\tilde{n}(\mathbf{r}) + \tilde{n}_{\text{core}}(\mathbf{r}) + \hat{n}_{\text{vale}}(\mathbf{r})]$$

Compensation charge; does not logically belong in this expression and can cause argument to be negative.

Densities fo Cs --



Binding energy curve for CsBr

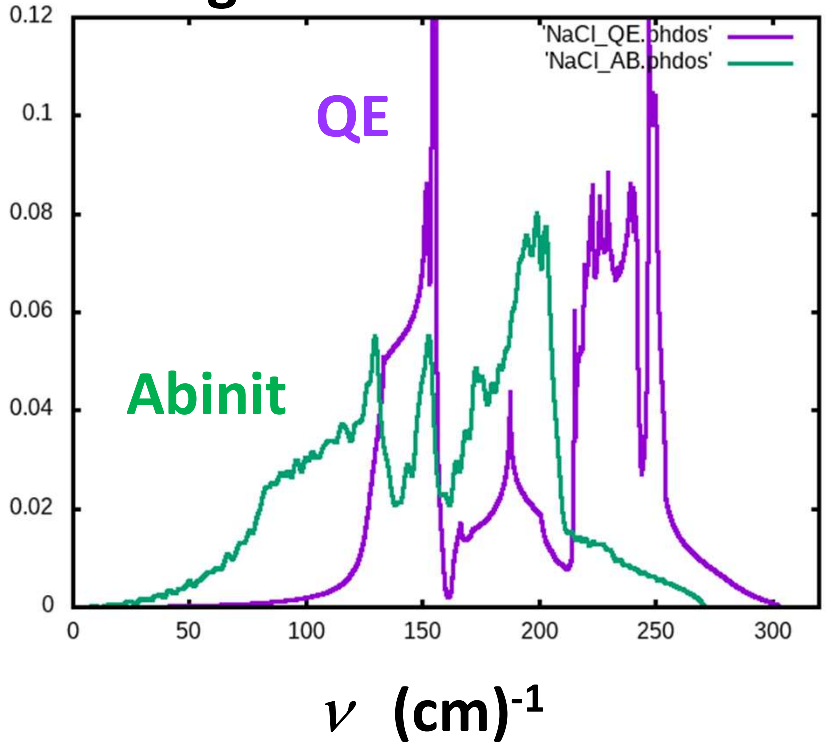


Other surprises due to the same issue

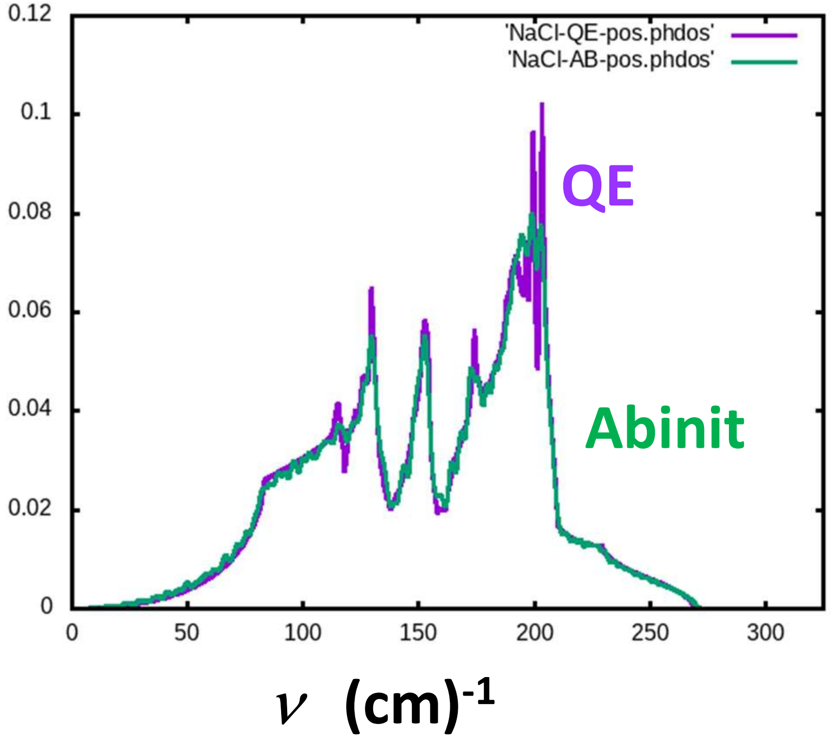
For NaCl, the electronic structure calculations performed with both QE and Abinit agreed well, but the density functional perturbation theory step resulted in incorrect phonon densities of states.

Phonon densities of states for NaCl

Original dataset for Cl



Corrected dataset for Cl



Summary and conclusions:

- Materials simulations is a mature field; there are many great ideas to use, but there still is plenty of room for innovation
- Maintain a skeptical attitude to the literature and to your own results
- Introduce checks into your work. For example, perform at least two independent calculations for a representative sample.
- On balance, static lattice results seem to be under good control. The next frontier is more accurate treatment of thermal effects and other aspects of representing macroscopic systems.
- Developing first-principles models of real materials to understand and predict their properties continues to challenge computational scientists.