SCIENCE'S COMPASS • PERSPECTIVES

PERSPECTIVES: DENSITY FUNCTIONAL THEORY

In Pursuit of the "Divine" Functional

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Paul Dirac reputedly said that the Schrödinger equation (SE) marked the end of chemistry: All answers could be calculated from the SE. The SE

lated exactly, just as the properties of small systems can be calculated from the SE.

The first step toward the divine functional was the local density approximation (LDA)

sively used in gas-phase catalysis, where the metallic character of the catalyst makes traditional SE methods inappropriate, and for determining phase diagrams (e.g., for steels).

In recognition of the importance of DFT, Walter Kohn was awarded half of the 1998 Nobel Prize in Chemistry (the other half was awarded to John Pople) (*10*). Today numerous approximate functionals are in use (*11*)—a sign of the method's utility but also an indication that none is suitable for all systems. As the complexity of systems investigated by DFT grows (see the figure), the task of choosing the right functional be-

Science **298**, 759 (2002)

Comparison shopping for a gradient-corrected density functional

John P. Perdew and Kieron Burke

Int. J. Quant. Chem. **57**, 309 (1996)

Parametrised local spin density exchange-correlation energies and potentials for electronic structure calculations

Computer Physics Communications **66**, 383 (1991)

DFT calculations for atoms

`http://www.nest.sns.it/~giannozz/Atom/Atom.tar.gz`

compile on Linux (g77)
run code `ld1`

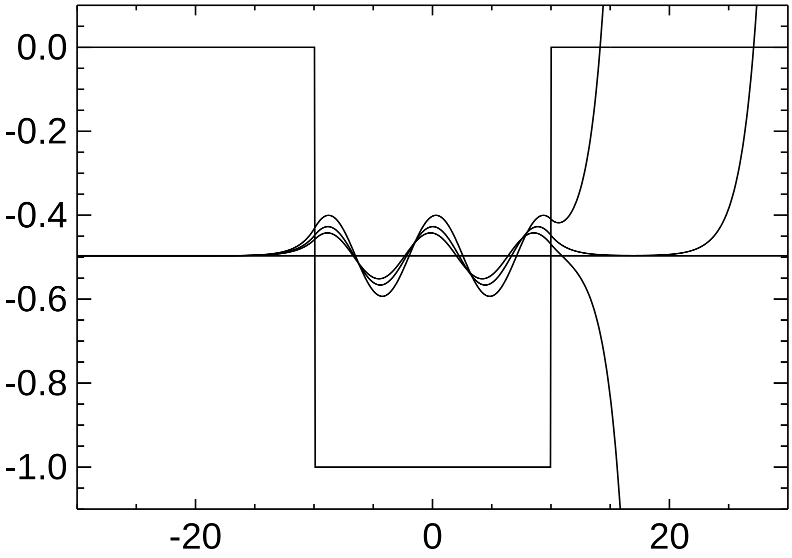
typical input (documented in `Src/ld1.f`)

```
&input
 atom='K',
 config='[Ar] 3d0 4s1.0 4p0 4d0',
 xmin=-8.0, dx=0.025, dft='vwn'
 file_wavefunctions='K.wfc'
&end
```

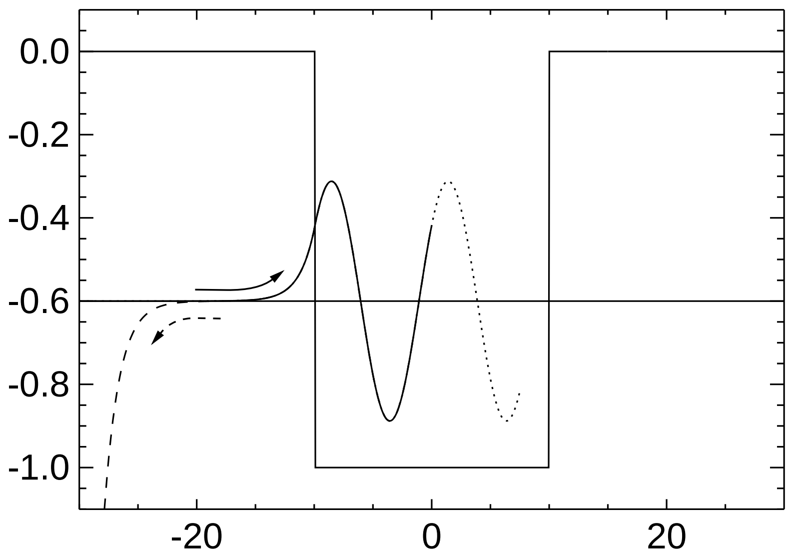
plot wavefunctions using `wfcgraf`
documentation (formulas etc.): `Doc/doc.tex`

check results against atomic reference data
`http://physics.nist.gov/PhysRefData/DFTdata/`

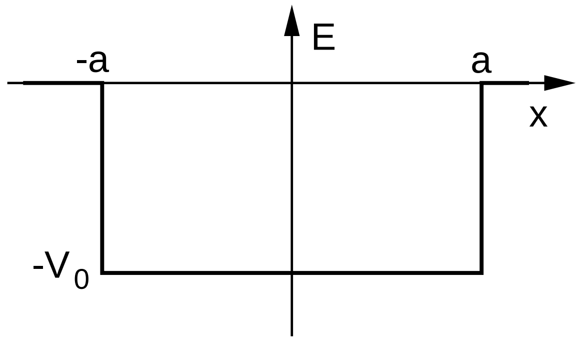
Numerov integration for energies close to an eigenvalue:



(in)stability of Numerov integration



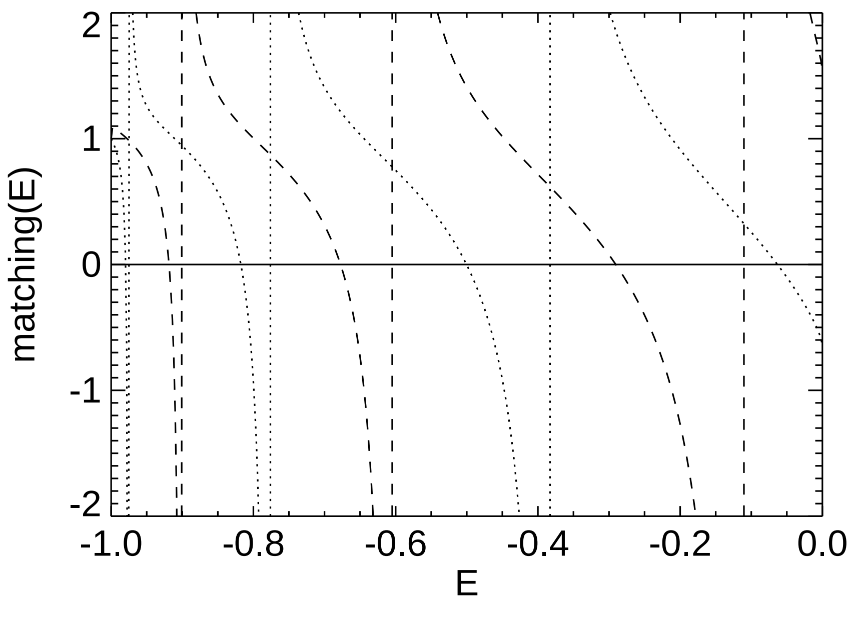
Square-well potential



$$a_0 = 10\,a_0 \quad V_0 = 1\,Ry$$

matching functions

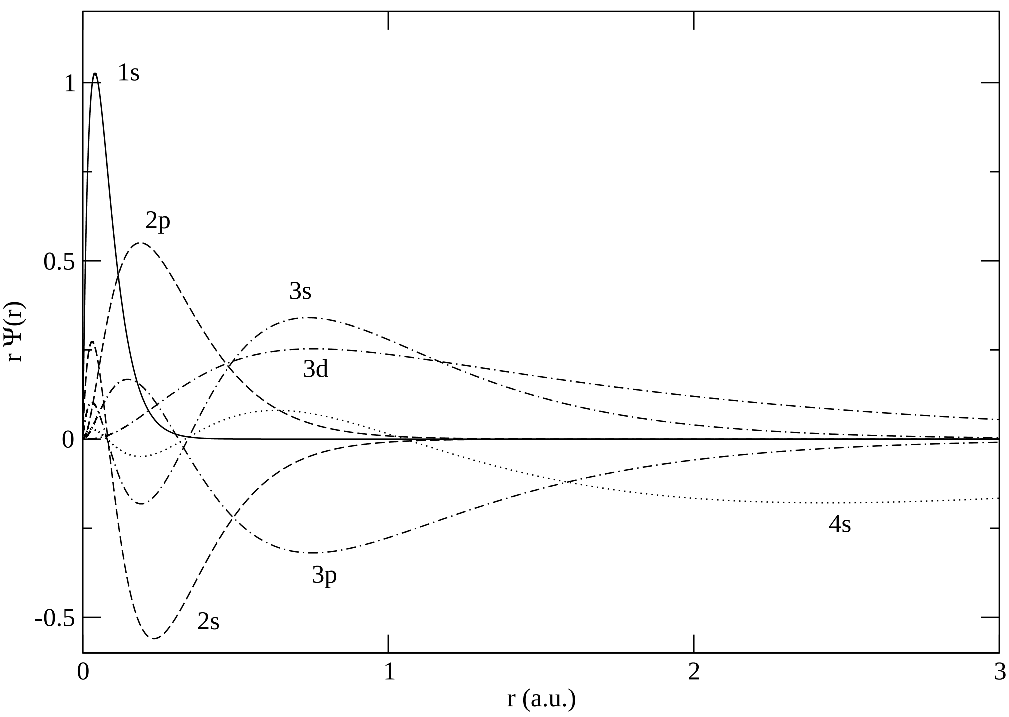
$$\text{matching}(E) \;=\; -k\,\tan(ka) + \kappa \;=\; 0 \quad \text{(even parity)}$$
$$\text{matching}(E) \;=\; k\,\cot(ka) + \kappa \;=\; 0 \quad \text{(odd parity)}$$



Core and Valence states

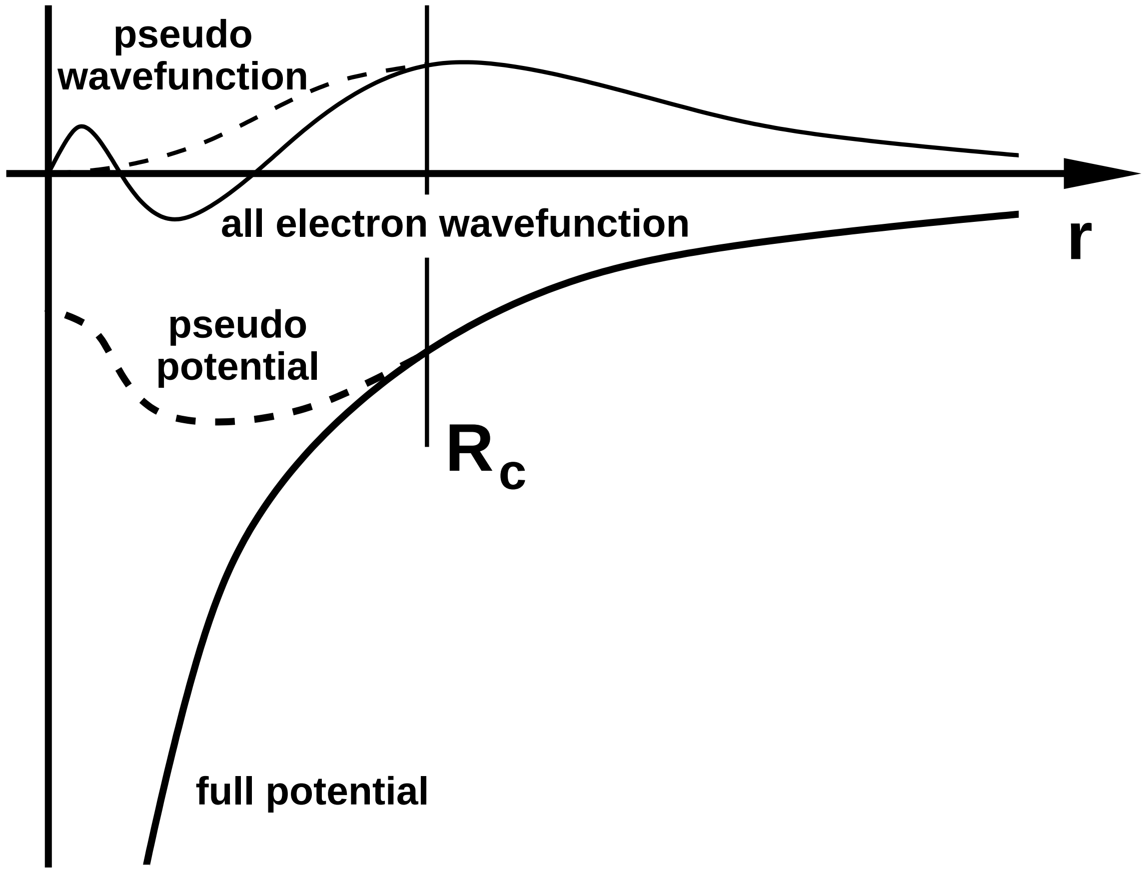
Manganese (Mn)

n	l	nl	e(Ry)	(eV)
1	0	1S(2.00)	-471.4645	-6414.6522
2	0	2S(2.00)	-54.5508	-742.2073
2	1	2P(6.00)	-46.2868	-629.7688
3	0	3S(2.00)	-6.2776	-85.4121
3	1	3P(6.00)	-4.0052	-54.4942
3	2	3D(5.00)	-0.5154	-7.0124
4	0	4S(2.00)	-0.3882	-5.2818
4	1	4P(0.00)	-0.1079	-1.4687



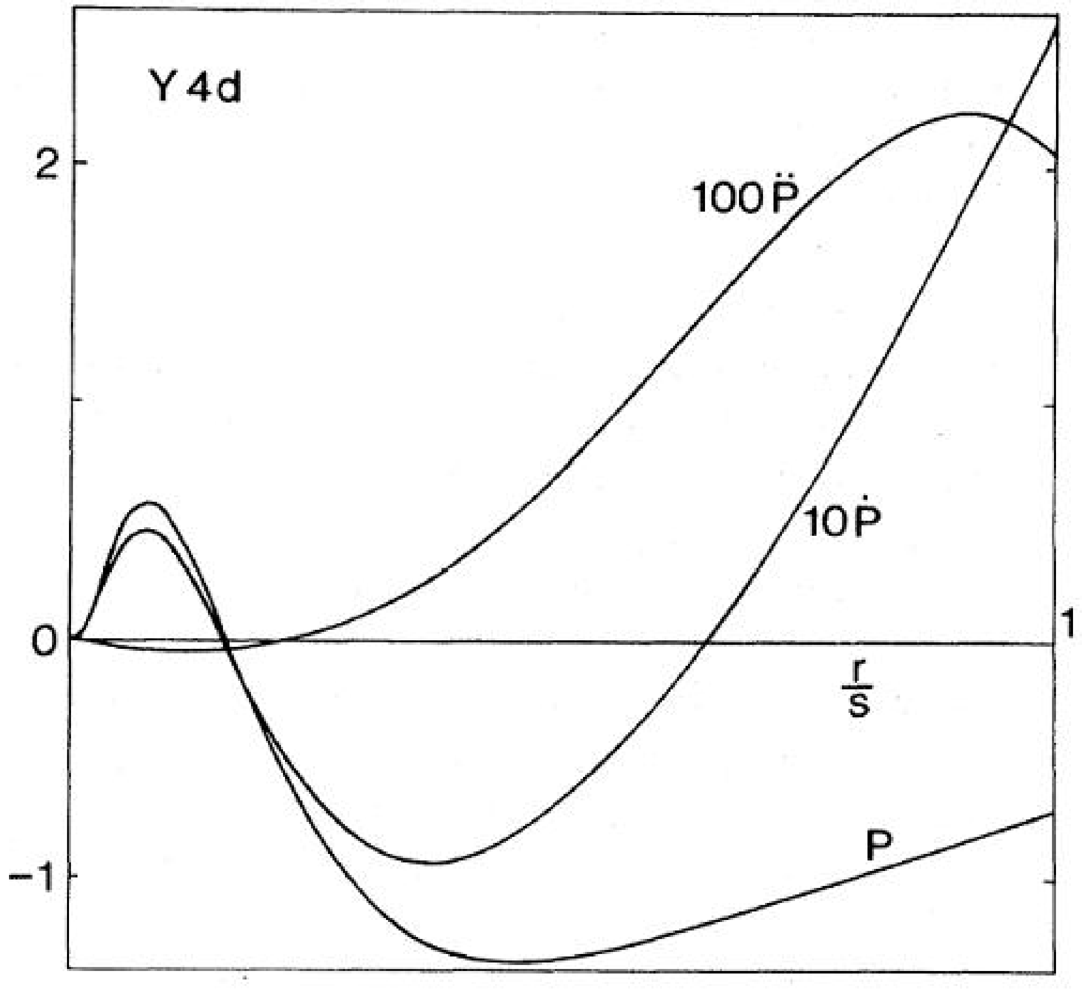
All-electron and Pseudopotential

logarithmic derivative on the atomic sphere



energy derivatives of radial function

radial d-function for Ytterbium



O.K. Andersen, Phys. Rev. B **12**, 3060 (1975)

DFT implementations

- all−electron full potential
- all−electron muffin−tin
- pseudopotential

- local density approximation (LDA)
- generalized grandient approx (GGA)
- beyond (OEP, SIC, LDA+U, GW)

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r}) + V_{xc}(\mathbf{r})\right)\,\phi_i(\mathbf{r}) = \varepsilon_i\,\phi_i(\mathbf{r})$$

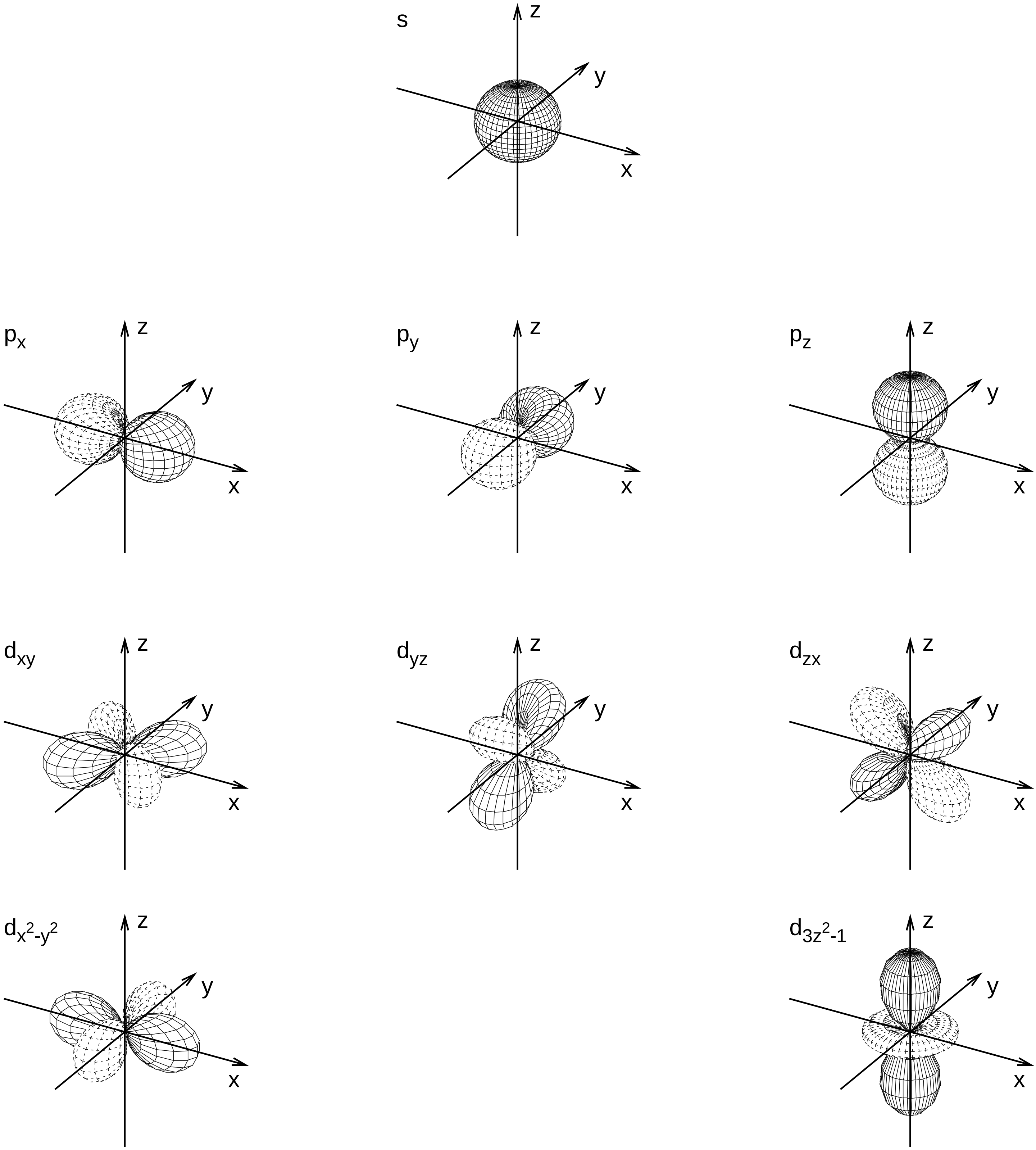
- plane waves
- augmented plane waves
- linearized APW
- atomic orbitals

real combinations of spherical harmonics

Notation	Spherical harmonics	Polar coordinates
s	$Y_{0,0}$	$\sqrt{\frac{1}{4\pi}}$
p_z	$Y_{1,0}$	$\sqrt{\frac{3}{4\pi}}\cos\theta$
p_x	$\sqrt{\frac{1}{2}}\left(Y_{1,-1}-Y_{1,1}\right)$	$\sqrt{\frac{3}{4\pi}}\sin\theta\cos\phi$
p_y	$\sqrt{\frac{1}{2}}i\left(Y_{1,-1}+Y_{1,1}\right)$	$\sqrt{\frac{3}{4\pi}}\sin\theta\sin\phi$
d_{3z^2-1}	$Y_{2,0}$	$\sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta-1\right)$
d_{zx}	$\sqrt{\frac{1}{2}}\left(Y_{2,-1}-Y_{2,1}\right)$	$\sqrt{\frac{15}{16\pi}}\sin 2\theta\cos\phi$
d_{yz}	$\sqrt{\frac{1}{2}}i\left(Y_{2,-1}+Y_{2,1}\right)$	$\sqrt{\frac{15}{16\pi}}\sin 2\theta\sin\phi$
$d_{x^2-y^2}$	$\sqrt{\frac{1}{2}}\left(Y_{2,-2}+Y_{2,2}\right)$	$\sqrt{\frac{15}{16\pi}}\sin^2\theta\cos 2\phi$
d_{xy}	$\sqrt{\frac{1}{2}}i\left(Y_{2,-2}-Y_{2,2}\right)$	$\sqrt{\frac{15}{16\pi}}\sin^2\theta\sin 2\phi$
$f_{z(5z^2-3)}$	$Y_{3,0}$	$\sqrt{\frac{7}{16\pi}}\left(5\cos^2\theta-3\right)\cos\theta$
$f_{x(5z^2-1)}$	$\sqrt{\frac{1}{2}}\left(Y_{3,-1}-Y_{3,1}\right)$	$\sqrt{\frac{21}{32\pi}}\left(5\cos^2\theta-1\right)\sin\theta\cos\phi$
$f_{y(5z^2-1)}$	$\sqrt{\frac{1}{2}}i\left(Y_{3,-1}+Y_{3,1}\right)$	$\sqrt{\frac{21}{32\pi}}\left(5\cos^2\theta-1\right)\sin\theta\sin\phi$
$f_{z(x^2-y^2)}$	$\sqrt{\frac{1}{2}}\left(Y_{3,-2}+Y_{3,2}\right)$	$\sqrt{\frac{105}{16\pi}}\cos\theta\sin^2\theta\cos 2\phi$
f_{xyz}	$\sqrt{\frac{1}{2}}i\left(Y_{3,-2}-Y_{3,2}\right)$	$\sqrt{\frac{105}{16\pi}}\cos\theta\sin^2\theta\sin 2\phi$
$f_{x(x^2-3y^2)}$	$\sqrt{\frac{1}{2}}\left(Y_{3,-3}-Y_{3,3}\right)$	$\sqrt{\frac{35}{32\pi}}\sin^3\theta\cos 3\phi$
$f_{y(3x^2-y^2)}$	$\sqrt{\frac{1}{2}}i\left(Y_{3,-3}+Y_{3,3}\right)$	$\sqrt{\frac{35}{32\pi}}\sin^3\theta\sin 3\phi$

Polar diagrams of s, p, d orbitals

absolute value, negative lobes are dashed



Polar diagrams of *f* orbitals

absolute value, negative lobes are dashed