Notes for Scalar-relativistic equations used in the *atompaw* code.

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The scalar-relativistic equations were originally developed by Koelling and Harmon[1] as a way to represent the physics of the Dirac equation, average over spin-orbit components. Another good reference for these equations is on the NIST website[2]
http://physics.nist.gov/PhysRefData/DFTdata/contents.html. In terms of Rydberg energy units (where the fine structure constant α is related to the speed of light according to $c = 2/\alpha$), the differential equation satisfied by upper component of the radial wavefunction ($G(r)/r$ with quantum number κ is

$$\left(\frac{d^2}{dr^2} - \frac{\kappa(\kappa+1)}{r^2}\right) G(r) + M(r)(E - V(r))G(r) - \frac{M'(r)}{M(r)}\left(\frac{d}{dr} + \frac{\langle\kappa\rangle}{r}\right) G(r) = 0. \tag{1}$$

Here,

$$M(r) \equiv 1 + \left(\frac{\alpha}{2}\right)^2 (E - V(r)). \tag{2}$$

The orbital angular momentum averaged value of κ is given by

$$\langle\kappa\rangle = \frac{1}{2(2\ell+1)}\left(\ell(2\ell) + (-\ell-1)(2\ell+2)\right) = -1. \tag{3}$$

Shadwick, Talman, and Normand[3] showed that it is possible to transform this equation into a form without the first derivative so that the Numerov integration scheme can be applied:

$$y(r) = \frac{G(r)}{\sqrt{M(r)}}, \tag{4}$$

with the resulting differential equation:

$$\frac{d^2}{dr^2} y(r) = A(r) y(r), \tag{5}$$

$$A(r) \equiv \frac{\kappa(\kappa+1)}{r^2} + (V(r) - E)M(r) + \frac{3}{4}\left(\frac{\alpha}{2}\right)^4 \left(\frac{1}{M(r)}\frac{dV(r)}{dr}\right)^2 \tag{6}$$

$$+\frac{1}{2}\left(\frac{\alpha}{2}\right)^2 \frac{1}{M(r)}\frac{d^2V(r)}{dr^2} + \left(\frac{\alpha}{2}\right)^2 \frac{1}{rM(r)}\frac{dV(r)}{dr}.$$

We have programmed these equations, and find that they work reasonably well with LDA exchange-correlation functionals, but for GGA functionals their sensitivity to the potential tends to lead to uncontrolled oscillations. Consequently, with the help of Marc Torrent and Francois Jollet of CEA, who modified a code of David Vanderbilt, we have developed the following alternate approach. In

the Vanderbilt code, the second-order scalar-relativistic code is written in terms of two coupled first order equations of the form:

$$\frac{d}{dr}G(r) = \frac{G(r)}{r} + M(r)F(r). \tag{7}$$

$$\frac{d}{dr}F(r) = -\frac{F(r)}{r} + \left(\frac{\kappa(\kappa+1)}{r^2}\frac{1}{M(r)} - (E - V(r))\right)G(r). \tag{8}$$

In these expressions, $F(r)$ is an auxiliary function which is similar to the radial function of the lower component in the Dirac equation. In this form, the scalar-relativistic equations are much more stable, since they do not directly use derivatives of the potential. Even with this approach, we find that the scalar-relativistic equations are sensitive to mesh size for the GGA exchange-correlation form. One approach for future implementations is to use a finite nuclear size model. This was done in the Vanderbilt code, although the details of the nuclear model are not obvious.

References

[1] D. D. Koelling and B. N. Harmon. A technique for relativisitic spin-polarised calculations. *Journal of Physics C: Solid State Physics*, 10:3107–3114, 1977.

[2] Svetlana Kotochigova, Zachary H. Levine, Eric L. Shirley, M. D. Stiles, and Charles W. Clark. Local-density-functional calculations of the energy of atoms. *Phys. Rev. A*, 55:191–199, 1997. This paper is the companion to the NIST database at the URL: http://physics.nist.gov/PhysRefData/DFTdata/contents.html.

[3] B. A. Shadwick, J. D. Talman, and M. R. Norman. A program to compute variationally optimized relativistic atomic potentials. *Computer Physics Communications*, 54:95–102, 1989.