Notes for Dirac equations and scalar-relativistic equations used in the *atompaw* code.

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Scalar-relativistic treatment

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 $c = 2/\alpha$). Explicitly, the constants expressed in SI units are as follows: $\alpha = e^2/(4\pi\epsilon_0\hbar c)$, the unit of length is the Bohr radius, $a_B = 4\pi\epsilon_0\hbar^2/(m_e e^2)$, and the Rydberg energy is $\varepsilon_{Ry} = \alpha^2 m_e c^2/2$). In these units, the differential equation satisfied by upper component of the radial wavefunction ($G(r)/r$ with quantum number κ is

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

Here,

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

Here we are interested in the spin-orbit splitting pair for each $\ell > 0$, where $\kappa = -\ell - 1 = -(j + \frac{1}{2})$ corresponds to $j = \ell + \frac{1}{2}$ and $\kappa = \ell = (j + \frac{1}{2})$ corresponds to $j = \ell - \frac{1}{2}$. 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:

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

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

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

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:

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

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

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. For a point nucleus, the electron-nucleus interaction has the singular form $-2Z/r$. In order to use the Vanderbilt code, it is necessary to to evaluate the wavefunction at several points at the origin and in the asymptotic regions. For $r \to 0$, we can make a power series expansion using

$$M(r) \underset{r\to 0}{\approx} 1 + \left(\frac{\alpha}{2}\right)^2 \left(\frac{2Z}{r} + E - V_0 - V_0' r\right) \tag{9}$$

The corresponding form of the radial wavefunctions near the origin takes the form

$$G(r) \underset{r\to 0}{\approx} r^\gamma \left(C_0 + C_1 r + C_2 r^2\right) \tag{10}$$

and, from Eq. (7) the corresponding auxiliary function takes the form

$$F(r) \underset{r\to 0}{\approx} \frac{r^\gamma}{rM(r)} \left(C_0(\gamma - 1) + C_1\gamma r + C_2(\gamma + 1)r^2\right). \tag{11}$$

In these expressions, the coeffients can be determined by analyzing Eq. (1) according to powers of r. For example,

$$M(r)(E - V(r)) \underset{r\to 0}{\approx} \frac{1}{r^2}\alpha^2 Z^2 + \frac{1}{r} Z\left(2 + \alpha^2(E - V_0)\right) + r^0 \left((E - V_0) + \frac{\alpha^2}{4}\left((E - V_0)^2 - 4ZV_0'\right)\right) .... \tag{12}$$

$$-\frac{M'(r)}{M(r)} \underset{r\to 0}{\approx} \frac{1}{r} + r^0 \left(-\frac{2}{Z\alpha^2}\left(1 + \frac{\alpha^2}{4}(E - V_0)\right)\right) + r^1 \left(\frac{4}{\alpha^2 Z^2} + \frac{V_0'}{Z} + \frac{E - V_0}{\alpha^2 Z^2}\left(2 + \frac{\alpha^2}{4}(E - V_0)\right)\right) + ... \tag{13}$$

The leading radial power coefficient is given by

$$\gamma = \sqrt{\ell(\ell+1) + 1 - Z^2\alpha^2}. \tag{14}$$

From the $r \to 0$ behavior of Eq. (1), the relationship between the coefficients C_n takes the general form:

$$T_n^{(-2)} C_n + T_n^{(-1)} C_{n-1} + T_n^{(0)} C_{n-2} = 0, \tag{15}$$

where

$$T_n^{(-2)} = n(2\gamma + n), \tag{16}$$

$$T_n^{(-1)} = Z(2 + \alpha^2(E - V_0)) - \frac{2}{\alpha^2 Z}\left(1 + \frac{\alpha^2}{4}(E - V_0)\right)(\gamma + n - 1), \tag{17}$$

and

$$T_n^{(0)} = -\alpha^2 Z V_0' + \left(1 + \frac{\alpha^2}{4}(E - V_0)\right)(E - V_0) + \left(\frac{V_0'}{Z} + \frac{4}{Z^2\alpha^4}\left(1 + \frac{\alpha^2}{4}(E - V_0)\right)^2\right)(\gamma + n - 1). \tag{18}$$

With these parameters, we can determine

$$C_1 = -\frac{T_0^{(-1)} C_0}{T_1^{(-2)}} \quad \text{and} \quad C_2 = -\frac{T_1^{(-1)} C_1 + T_0^{(0)} C_0}{T_2^{(-2)}}. \tag{19}$$

The code also implements several finite nuclear models described by Andrae[4] which has no singular behavior at the origin. For the finite nuclear models, the singular electron-nuclear term is omitted, while the values of the potential constants V_0 and V_0' are adjusted accordingly. In this case, we can use the same small r expansions as in Eqs. 10 and 11, using the recursion formulas Eq. (19), however the parameters are altered to

$$\gamma \to \tilde{\gamma} = \ell + 1. \tag{20}$$

$$T_n^{(-2)} \to \tilde{T}_n^{(-2)} = n(2\ell + 1 + n). \tag{21}$$

$$T_n^{(-1)} \to \tilde{T}_n^{(-1)} = \frac{\alpha^2}{4} V_0' \left(\frac{1}{\left(1 + \frac{\alpha^2}{4}(E - V_0)\right)}\right)(\ell + n). \tag{22}$$

$$T_n^{(0)} \to \tilde{T}_n^{(0)} = (E - V_0)\left(1 + \frac{\alpha^2}{4}(E - V_0)\right) + \left(\frac{\alpha^2}{4} V_0' \left(\frac{1}{\left(1 + \frac{\alpha^2}{4}(E - V_0)\right)}\right)\right)^2 (\ell + n). \tag{23}$$

Note that these equations are slightly inconsistent with the scalarrelativistic code versions $< 4.0.1.0$ for the C_2 coefficients. In order to find bound states ($0 > E \equiv -b^2$, the solver requires inward integration from $r_{\max}$. Here, we assume that the potential vanishes up to a possible (positive) Coulombic charge of qe so that

$$V(r) \underset{r\to\infty}{\approx} -\frac{2q}{r}. \tag{24}$$

Then the asymptotic form of the radial wavefunctions are

$$G(r) \underset{r\to\infty}{\approx} \mathrm{e}^{-br} r^g, \quad \text{and} \quad F(r) \underset{r\to\infty}{\approx} \left(-b + \frac{g-1}{r}\right)\frac{G(r)}{M(r)}, \tag{25}$$

where

$$b \equiv \sqrt{|E|\left(1 - \frac{\alpha^2|E|}{4}\right)}, \tag{26}$$

and

$$g \equiv \frac{q}{b}\left(1 - \frac{\alpha^2}{2}|E|\right). \tag{27}$$

Full Dirac treatment

It is also possible to analyze the full Dirac equation in a similar way. For this, we follow the convention of Loucks[5] and define the function

$$cF(r) \equiv \frac{2}{\alpha} F(r). \tag{28}$$

The function $cF(r)$ is used for input to and within the subroutine unboundD and boundD, but the output lower component wave function is $F(r)$. The coupled equations for the full Dirac radial functions in Rydberg energy units then become

$$\left(\frac{d}{dr}+\frac{\kappa}{r}\right)G(r)=\left(1+\left(\frac{\alpha}{2}\right)^2(E-V(r))\right)cF(r) \tag{29}$$

and

$$\left(\frac{d}{dr}-\frac{\kappa}{r}\right)cF(r)=-\left(E-V(r)\right)G(r) \tag{30}$$

In order to determine the form of the radial wavefunctions in the limit as $r\to 0$, we again expand the potential as a power series in r:

$$V(r)\underset{r\to 0}{\approx}-\frac{2Z}{r}+V_0, \tag{31}$$

and also represent the upper and lower radial wavefunctions in a power series with leading power coefficient r^s:

$$G(r)\underset{r\to 0}{\approx}r^s\sum_{n=0}^{\infty}A_nr^n\qquad cF(r)\underset{r\to 0}{\approx}r^s\sum_{n=0}^{\infty}B_nr^n. \tag{32}$$

A recursion formula for the coefficients takes the form

$$\begin{pmatrix} s+n+\kappa & -Z\alpha^2/2 \\ 2Z & s+n-\kappa \end{pmatrix}\begin{pmatrix} A_n \\ B_n \end{pmatrix}=\begin{pmatrix} 0 & 1+\alpha^2(E-V_0)/4 \\ -(E-V_0) & 0 \end{pmatrix}\begin{pmatrix} A_{n-1} \\ B_{n-1} \end{pmatrix}. \tag{33}$$

The condition for a non-trivial solution fixes the value of the leading power s:

$$s=\sqrt{\kappa^2-Z^2\alpha^2}, \tag{34}$$

and the corresponding ratio of the leading coefficients is given by

$$B_0=\frac{2(s+\kappa)}{Z\alpha^2}A_0. \tag{35}$$

From evaluating Eq. (19), the first order coefficients can be computed to be

$$A_1=\frac{4\alpha^4Z^2+\left(4\alpha^2+E-V_0\right)\left((s+\kappa)-2\alpha^2Z^2\right)}{2Z(2s+1)}A_0, \tag{36}$$

and

$$B_1=-\frac{\left(2\alpha^2+E-V_0\right)\left(2(s+\kappa)+(E-V_0)\right)}{(2s+1)}A_0. \tag{37}$$

With these results, we can use the following relationships to initialize the radial wavefunctions near the origin:

$$G(r)\underset{r\to 0}{\approx}r^s(A_0+A_1r)\quad\text{and}\quad cF(r)\underset{r\to 0}{\approx}r^s(B_0+B_1r). \tag{38}$$

Note that for the case of a finite potential model or a pseudopotential where $Z=0$ in Eq. (31), this analysis has to be re-examined since the expansion coefficients diverge.

For evaluating the aymptotic form, we can assume that the potential vanishes so that the upper component satisfies the equation

$$\left(\frac{d^2}{dr^2}-\frac{\ell(\ell+1)}{r^2}-b^2\right)G(r)=0, \tag{39}$$

where

$$b = \sqrt{|E|\left(1 - \frac{\alpha^2}{4}|E|\right)} \tag{40}$$

and $\ell = \kappa$ for $\kappa > 0$ and and $\ell = -\kappa - 1$ for $\kappa < 0$. We can thus assume the asymptotic solution form:

$$G_{n\kappa}(r) \underset{r\to\infty}{\approx} k_\ell(br), \tag{41}$$

where $k_\ell(u)$ denotes u times a modified bessel function of the third kind, having the values

$$k_0(u) = \mathrm{e}^{-u} \quad k_1(u) = \mathrm{e}^{-u}\left(1 + \frac{1}{u}\right) \quad k_2(u) = \mathrm{e}^{-u}\left(1 + \frac{3}{u} + \frac{3}{u^2}\right), \tag{42}$$

etc. These functions can be generated according to the recurrsion relation[6]

$$k_{\ell+2}(u) = k_\ell(u) + \frac{(2\ell+3)}{u} k_{\ell+1}(u). \tag{43}$$

From the recurrsion relations[6], one can also show that

$$\left(\frac{d}{du} + \frac{\ell}{u}\right) k_\ell(u) = -k_{\ell-1}(u), \tag{44}$$

which can be used to obtain the asymptotic form of the lower component

$$cF_{n\kappa}(r) \underset{r\to\infty}{\approx} -\frac{|E|}{b} k_{\ell-1}(br). \tag{45}$$

Note that the text, *Atomic Structure Theory: Lectures on Atomic Physics* by Johnson[7] gives many more details on the asymptotic forms and a later version of this code should include those results. At the moment, the code only includes the leading terms quoted here and will not work for an ion. Johnson[7] also works out a very clever method of converging the energy eigenvalues from the inward and outward integration. In particular, he noted that the solutions of Eq. (29) with labels 1 and 2 corresponding to energies E_1 and E_2 have the identity:

$$\frac{d}{dr}(G_1\ cF_2 - G_2\ cF_1) = (E_1 - E_2)\left(\frac{\alpha^2}{4} cF_1\ cF_2 + G_1 G_2\right). \tag{46}$$

In a similar way that Hartree[8] used the mismatch of the slope of the inward and outward integration results to adjust the energy, Eq. (46) can be used to correct the energy. At the matching radius r_m, we normalize the upper component so that $G_{\rm out}(r_m) = G_{\rm in}(r_m)$, but the corresponding lower component will have a discontinuity $\Delta[cF(r_m)] \equiv cF_{\rm out}(r_m) - cF_{\rm in}(r_m)$. The first order estimate of the energy correction is thus given by

$$\Delta E = C\ G(r_m)\Delta[cF(r_m)], \quad \text{where} \quad C^{-1} \equiv \int_0^\infty \left((G(r))^2 + \frac{\alpha^2}{4}(cF(r))^2\right). \tag{47}$$

In order to test whether the code is working, it is helpful to check the analytic solutions for a H-like ion with nuclear charge Z, which is given in the textbook by Bethe and Saltpeter[9] and can be expressed in terms of confluent hypergeometric polynomial (Kummer) functions[6] $F(a, b, z)$, the principal quantum number

$$n = |\kappa|, |\kappa| + 1, |\kappa| + 2, ... \equiv n' + |\kappa|, \tag{48}$$

the apparent principal quantum number

$$N \equiv \sqrt{n^2 - 2n'(|\kappa| - s)}, \tag{49}$$

the normalization factor

$$\mathcal{N} \equiv \sqrt{\frac{\Gamma(2s + n' + 1)}{(n'!)4N(N - \kappa)}} \frac{1}{\Gamma(2s + 1)} \left(\frac{2Z}{N}\right)^{1/2}, \tag{50}$$

and the length parameter (in Bohr units)

$$\rho \equiv \frac{2Zr}{N}. \tag{51}$$

In terms of the previously defined parameters, including the energy E relative to the electron rest mass energy (in Rydberg energy units), the normalized radial wavefunctions take the form (up to an arbitrary sign convention)

$$G_{n\kappa}(r) = \mathcal{N}\sqrt{\left(2 + \frac{\alpha^2}{2}E_{n\kappa}\right)}\, \mathrm{e}^{-\rho/2}\rho^s \left((N - \kappa)F(-n', 2s + 1, \rho) - n'F(-n' + 1, 2s + 1, \rho)\right) - \tag{52}$$

and

$$F_{n\kappa}(r) = -\mathcal{N}\sqrt{\left(-\frac{\alpha^2}{2}E_{n\kappa}\right)}\, \mathrm{e}^{-\rho/2}\rho^s \left((N - \kappa)F(-n', 2s + 1, \rho) + n'F(-n' + 1, 2s + 1, \rho)\right). \tag{53}$$

The energy eigenvalue $E_{n\kappa} < 0$ is given by:

$$E_{n\kappa} = \frac{2}{\alpha^2}\left(\left(1 + \frac{\alpha^2 Z^2}{(n - |\kappa| + s)^2}\right)^{-1/2} - 1\right). \tag{54}$$

In order to take advantage of the solver properties, it is convenient to calculate all of the bound states for each κ value. These are called in the order of $\kappa = -1, 1, -2, 2, -3, 3, -4..$ corresponding to orbital angular momenta of the upper component $\ell = 0, 1, 1, 2, 2, 3, 3, ...$ If another ordering is desired, this can easily be accomplished with the use of a mapping algorithm.

Example input and output

At the moment, only graphatom is programmed to use the Dirac equation solver. To run graphatom, use the following command in a directory containing the "in" file:

```
[path]/bin/graphatom<in>&out&
```

An example "in" file for Bi is:

```
Bi  83
LDA-PW  diracrelativistic loggrid    2001
6 6 5 4 0 0
6 1 1 2
6 1 -2 1
0 0 0 0
0
```

The corresponding Bi.GA file is:

```
 Completed calculations for Bi
 Perdew-Wang LDA -- PRB 45, 13244 (1992)
  Radial integration grid is logarithmic
r0 =   8.3003918E-05 h =   6.8893252E-03   n =      2001 rmax =   8.0000000E+01
 Dirac-relativistic calculation
   AEatom converged in          29  iterations
     for nz =  83
     delta  =   3.313784838079538E-016

 Orbital energies
 n   kappa   l   occupancy            energy
 1 -1   0      2.0000000E+00 -6.6480533E+03
 2 -1   0      2.0000000E+00 -1.1934355E+03
 3 -1   0      2.0000000E+00 -2.8796157E+02
 4 -1   0      2.0000000E+00 -6.5980525E+01
 5 -1   0      2.0000000E+00 -1.1514073E+01
 6 -1   0      2.0000000E+00 -1.0379038E+00
 2  1   1      2.0000000E+00 -1.1468243E+03
 3  1   1      2.0000000E+00 -2.6688214E+02
 4  1   1      2.0000000E+00 -5.6821818E+01
 5  1   1      2.0000000E+00 -8.3277130E+00
 6  1   1      2.0000000E+00 -4.2545518E-01
 2 -2   1      4.0000000E+00 -9.7647279E+02
 3 -2   1      4.0000000E+00 -2.2874691E+02
 4 -2   1      4.0000000E+00 -4.7404690E+01
 5 -2   1      4.0000000E+00 -6.4975188E+00
 6 -2   1      1.0000000E+00 -2.8622974E-01
 3  2   2      4.0000000E+00 -1.9414140E+02
 4  2   2      4.0000000E+00 -3.2493774E+01
 5  2   2      4.0000000E+00 -2.0654190E+00
 3 -3   2      6.0000000E+00 -1.8605221E+02
 4 -3   2      6.0000000E+00 -3.0736387E+01
 5 -3   2      6.0000000E+00 -1.8441098E+00
 4  3   3      6.0000000E+00 -1.1362662E+01
 4 -4   3      8.0000000E+00 -1.0958823E+01

  Total energy
     Total                    :    -46803.6120503352
```

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[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`.

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