PHY 742 Quantum Mechanics
12:00-12:50 PM MWF Olin 103

Plan for Lecture 20:
Dirac equation for hydrogen-like ions and other atoms

Chap. 16 in Carlson's text – Supplemented with J. J. Sakurai, Advanced QM

1. Review of results for H-like ions
2. Generalization to approximate treatment of spherical atoms
3. Comparison with non-relativistic results

16	Wed: 02/23/2022	Chap. 16	The Dirac equation	#14	02/25/2022
17	Fri: 02/25/2022	Chap. 16	The Dirac equation	#15	02/28/2022
18	Mon: 02/28/2022	Chap. 16	The Dirac equation	#16	03/02/2022
19	Wed: 03/02/2022	Chap. 16	The Dirac equation		
20	Fri: 03/04/2022	Chap. 16	The Dirac equation		
	Mon: 03/07/2022	No class	*Spring Break*		
	Wed: 03/09/2022	No class	*Spring Break*		
	Fri: 03/11/2022	No class	*Spring Break*		
	Mon: 03/14/2022	No class	*APS March Meeting*	Prepare Project	
	Wed: 03/16/2022	No class	*APS March Meeting*	Prepare Project	
	Fri: 03/18/2022	No class	*APS March Meeting*	Prepare Project	
	Mon: 03/21/2022		Project presentations I		
	Wed: 03/23/2022		Project presentations II		
21	Fri: 03/25/2022				

Dirac equation for electron in a scalar, spherically symmetric potential *V(r)*

$$H\Psi = \begin{pmatrix} mc^2 + V(r) & \mathbf{p}\cdot\boldsymbol{\sigma}c \\ \mathbf{p}\cdot\boldsymbol{\sigma}c & -mc^2 + V(r) \end{pmatrix}\begin{pmatrix} \varphi^U(\mathbf{r}) \\ \varphi^L(\mathbf{r}) \end{pmatrix} = E\begin{pmatrix} \varphi^U(\mathbf{r}) \\ \varphi^L(\mathbf{r}) \end{pmatrix} = E\Psi$$

This Hamiltonian commutes with the operators $\mathbf{J}^2, J_z$, and K: $\left|JM\right\rangle$

$$\mathbf{J}^2\left|\kappa JM\right\rangle = \hbar^2 J(J+1)\left|\kappa JM\right\rangle$$

$$J_z\left|\kappa JM\right\rangle = \hbar M\left|\kappa JM\right\rangle$$

$$K\left|\kappa JM\right\rangle = -\hbar\kappa\left|\kappa JM\right\rangle$$

We can show that:

$$\begin{pmatrix} \varphi^U(\mathbf{r}) \\ \varphi^L(\mathbf{r}) \end{pmatrix} = \begin{pmatrix} g_{\kappa J}(r)\chi_{\kappa JM}(\hat{\mathbf{r}}) \\ if_{\kappa J}(r)\chi_{-\kappa JM}(\hat{\mathbf{r}}) \end{pmatrix} = \begin{pmatrix} G_{\kappa J}(r)/r\,\chi_{\kappa JM}(\hat{\mathbf{r}}) \\ iF_{\kappa J}(r)/r\,\chi_{-\kappa JM}(\hat{\mathbf{r}}) \end{pmatrix}$$

Coupled differential equations for radial functions:

$$\left(V(r)+mc^2-E\right)G_{E\kappa J}(r)=\hbar c\left(\frac{d}{dr}+\frac{-\kappa}{r}\right)F_{E\kappa J}(r)$$

$$\left(V(r)-mc^2-E\right)F_{E\kappa J}(r)=-\hbar c\left(\frac{d}{dr}+\frac{\kappa}{r}\right)G_{E\kappa J}(r)$$

Summary of allowed combinations of eigenvalues

	l_U	l_L
$\kappa = -\left(J+\frac{1}{2}\right)$	$J-\frac{1}{2}$	$J+\frac{1}{2}$
$\kappa = +\left(J+\frac{1}{2}\right)$	$J+\frac{1}{2}$	$J-\frac{1}{2}$

Alternatively

	J	l_L
$\kappa = -\left(l_U+1\right)$	$l_U+\frac{1}{2}$	l_U+1
$\kappa = +l_U$	$l_U-\frac{1}{2}$	l_U-1

Note that for stationary state solutions to the Dirac equation $H\Psi_{E\kappa JM} = E\Psi_{E\kappa JM}$, the κ value is identified with φ^U.

$$\Psi_{E\kappa JM} = \begin{pmatrix} \varphi^U(\mathbf{r}) \\ \varphi^L(\mathbf{r}) \end{pmatrix} = \begin{pmatrix} g_{E\kappa J}(r)\chi_{\kappa JM}(\hat{\mathbf{r}}) \\ if_{E\kappa J}(r)\chi_{-\kappa JM}(\hat{\mathbf{r}}) \end{pmatrix} = \begin{pmatrix} G_{E\kappa J}(r)/r\,\chi_{\kappa JM}(\hat{\mathbf{r}}) \\ iF_{E\kappa J}(r)/r\,\chi_{-\kappa JM}(\hat{\mathbf{r}}) \end{pmatrix}$$

Combinations:

$\kappa = -1$	$J = \frac{1}{2}$	$l_U = 0$	$l_L = 1$
$+1$	$\frac{1}{2}$	1	0
-2	$\frac{3}{2}$	1	2
$+2$	$\frac{3}{2}$	2	1
-3	$\frac{5}{2}$	2	3
$+3$	$\frac{5}{2}$	3	2

For the case of a H-like ion with atomic number Z :

$$V(r) = -\frac{Ze^2}{r}$$

Fine-structure constant:

$$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137.035999139}$$

Exact solution of Dirac equation for H-like ion:

$$E_n = \frac{mc^2}{\left(1 + \dfrac{Z^2\alpha^2}{\left(\left(\left(J+\frac{1}{2}\right)^2 - Z^2\alpha^2\right)^{1/2} - \left(J+\frac{1}{2}\right) + n\right)^2}\right)^{1/2}}$$

for $n = \left(J+\frac{1}{2}\right), \left(J+\frac{1}{2}+1\right), \left(J+\frac{1}{2}+2\right), \ldots$

Dirac equation for electron in the field of a H-like ion

Comparison with Schrödinger equation --

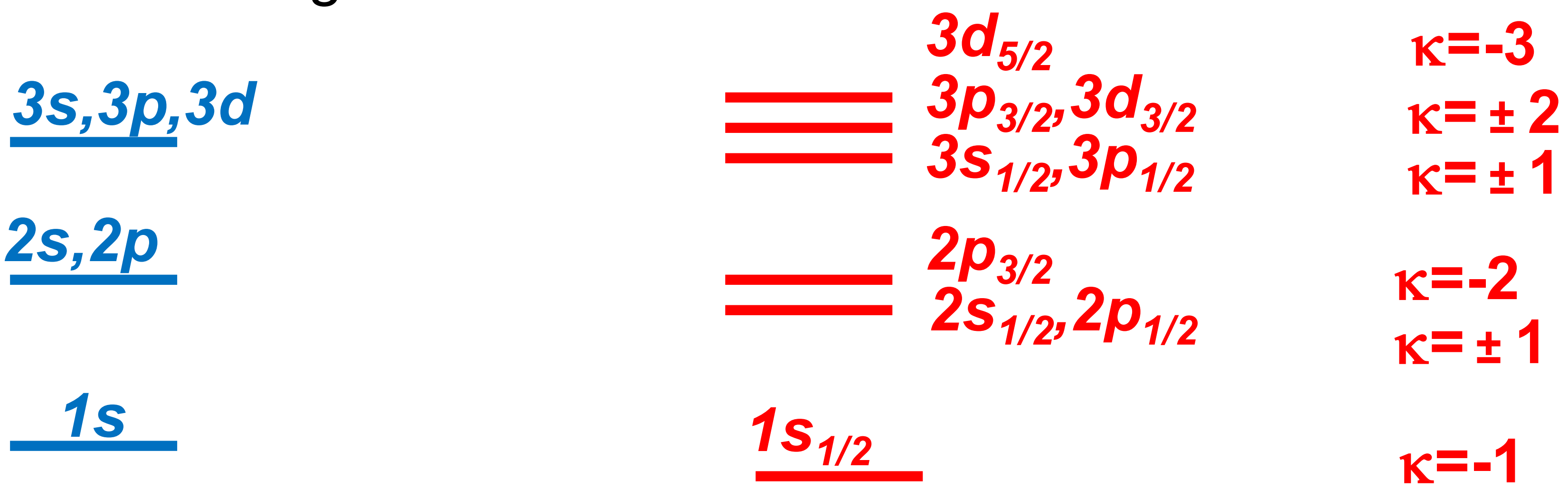
Schrödinger equation

$$E_n^{Sch} = -\frac{Z^2\alpha^2 mc^2}{2n^2}$$

Dirac equation

$$E_n^{Dir} - mc^2 \approx -\frac{Z^2\alpha^2 mc^2}{2n^2}\left(1 + \frac{Z^2\alpha^2}{n}\left(\frac{1}{J+\frac{1}{2}} - \frac{3}{4n}\right)....\right)$$

Schematic diagram:



Physical differences due to Dirac equation on the H-like ions

Dirac equation

α^{-1}=137.035999084
mc^2=510998.950 eV

$$E_{nJ} - mc^2 \approx -\frac{Z^2\alpha^2 mc^2}{2n^2}\left(1+\frac{Z^2\alpha^2}{n}\left(\frac{1}{J+\frac{1}{2}}-\frac{3}{4n}\right)....\right)$$

For $J=\frac{1}{2}$ and $n=1$

$$E_{1\frac{1}{2}} - mc^2 \approx -\frac{Z^2\alpha^2 mc^2}{2}\left(1+\frac{Z^2\alpha^2}{4}\right) =\approx -13.6057 \text{ eV } Z^2\left(1+\frac{Z^2\alpha^2}{4}\right)$$

$\Rightarrow$ Dirac equation describes an additional attractive energy for the ground state which can explained by fluctuations with the negative energy solutions analyzed by C. G. Darwin.

Physical differences due to Dirac equation on the H-like ions

Dirac equation

$$E_{nJ} - mc^2 \approx -\frac{Z^2\alpha^2 mc^2}{2n^2}\left(1+\frac{Z^2\alpha^2}{n}\left(\frac{1}{J+\frac{1}{2}}-\frac{3}{4n}\right)....\right)$$

Spin-orbit splitting:

$$E_{n(J+1)} - E_{nJ} \approx \frac{Z^4\alpha^4 mc^2}{2n^3}\frac{1}{(J+\frac{1}{2})(J+\frac{3}{2})}$$

Some details

Exact solution of Dirac equation for H-like ion:

$$E_n = \frac{mc^2}{\left(1+\dfrac{Z^2\alpha^2}{\left(\left(\left(J+\frac{1}{2}\right)^2 - Z^2\alpha^2\right)^{1/2} - \left(J+\frac{1}{2}\right)+n\right)^2}\right)^{1/2}}$$

for $n=1$ and $J=\frac{1}{2}$:

$$E_1 = mc^2\sqrt{1-Z^2\alpha^2}$$

More details about ground state of H-like ion from Dirac equation

$$n=1 \quad J=\tfrac{1}{2} \qquad \kappa=-1$$

$$E_1 = mc^2\sqrt{1-Z^2\alpha^2} \qquad s=\sqrt{1-Z^2\alpha^2} \qquad \sqrt{\epsilon_1\epsilon_2}=\frac{Z\alpha mc^2}{\hbar c}=\frac{Z}{a_0}$$

$$\begin{pmatrix} \varphi^U(\mathbf{r}) \\ \varphi^L(\mathbf{r}) \end{pmatrix} = \mathcal{N}\left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr/a_0} r^{s-1} \begin{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ i\dfrac{D_0}{C_0}(\boldsymbol{\sigma}\cdot\hat{\mathbf{r}})\begin{pmatrix} 1 \\ 0 \end{pmatrix} \end{pmatrix}$$

$$\text{where } \frac{D_0}{C_0}=\frac{1-s}{Z\alpha} \qquad \text{Degenerate with } \begin{pmatrix} 1 \\ 0 \end{pmatrix} \leftrightarrow \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Practical solution of radial portions of Dirac equation

$$\left(V(r)+mc^2-E\right)g_{E\kappa J}(r)=\hbar c\left(\frac{d}{dr}+\frac{-\kappa+1}{r}\right)f_{E\kappa J}(r)$$

$$\left(V(r)-mc^2-E\right)f_{E\kappa J}(r)=-\hbar c\left(\frac{d}{dr}+\frac{\kappa+1}{r}\right)g_{E\kappa J}(r)$$

Let $g_{E\kappa J}(r)=G_{E\kappa J}(r)/r$ and $f_{E\kappa J}(r)=F_{E\kappa J}(r)/r$

$$\left(\frac{d}{dr}+\frac{\kappa}{r}\right)G_{E\kappa J}(r)=\frac{1}{\hbar c}\left(E+mc^2-V(r)\right)F_{E\kappa J}(r)$$

$$\left(\frac{d}{dr}-\frac{\kappa}{r}\right)F_{E\kappa J}(r)=-\frac{1}{\hbar c}\left(E-mc^2-V(r)\right)G_{E\kappa J}(r)$$

More general treatment of bound states of Fermi particle within spherical potential *V(r)* -- continued

$$\left(\frac{d}{dr}+\frac{\kappa}{r}\right)G_{E\kappa J}(r) \;=\frac{1}{\hbar c}\Big(E+mc^2-V(r)\Big)F_{E\kappa J}(r)$$

$$\left(\frac{d}{dr}-\frac{\kappa}{r}\right)F_{E\kappa J}(r) \;=-\frac{1}{\hbar c}\Big(E-mc^2-V(r)\Big)G_{E\kappa J}(r)$$

Note that for an electron, $mc^2 = 0.511\times 10^6$ eV

If we can assume that $V(r) \ll mc^2$, then the equations simplify:

$$\left(\frac{d}{dr}+\frac{\kappa}{r}\right)G_{E\kappa J}(r) \;\approx \frac{2mc^2}{\hbar c}F_{E\kappa J}(r)$$

And then we can replace $F_{E\kappa J}(r)$ in the second equation:

$$\left(\frac{d}{dr}-\frac{\kappa}{r}\right)\left(\frac{d}{dr}+\frac{\kappa}{r}\right)G_{E\kappa J}(r) \;=-\frac{2mc^2}{\hbar c}\frac{1}{\hbar c}\Big(E-mc^2-V(r)\Big)G_{E\kappa J}(r)$$

More general treatment of bound states of Fermi particle within spherical potential *V(r)* -- continued

Approximate radial equation for upper component

$$\left(\frac{d}{dr}-\frac{\kappa}{r}\right)\left(\frac{d}{dr}+\frac{\kappa}{r}\right)G_{E\kappa J}(r) \;=-\frac{2mc^2}{\hbar c}\frac{1}{\hbar c}\left(E-mc^2-V(r)\right)G_{E\kappa J}(r)$$

$$\left(-\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2}-\frac{\kappa(\kappa+1)}{r^2}\right)+V(r)\right)G_{E\kappa J}(r)=\left(E-mc^2\right)G_{E\kappa J}(r)$$

$$F_{E\kappa J}(r)\approx\frac{\hbar c}{2mc^2}\left(\frac{d}{dr}+\frac{\kappa}{r}\right)G_{E\kappa J}(r)$$

More general treatment of bound states of Fermi particle within spherical potential *V(r)* -- continued

Full eigenfunction:

$$\Psi_{E\kappa J}(\mathbf{r}) = \begin{pmatrix} \left(G_{E\kappa J}(r)/r\right)\chi_{\kappa JM}(\hat{\mathbf{r}}) \\ \left(iF_{E\kappa J}(r)/r\right)\chi_{-\kappa JM}(\hat{\mathbf{r}}) \end{pmatrix}$$

$$\left(\frac{d}{dr}+\frac{\kappa}{r}\right)G_{E\kappa J}(r) \;= \frac{1}{\hbar c}\left(E+mc^2-V(r)\right)F_{E\kappa J}(r)$$

$$\left(\frac{d}{dr}-\frac{\kappa}{r}\right)F_{E\kappa J}(r) \;= -\frac{1}{\hbar c}\left(E-mc^2-V(r)\right)G_{E\kappa J}(r)$$

Choosing the non-relativistic zero of energy: $E^{NR} \equiv E - mc^2$

$$\left(\frac{d}{dr}+\frac{\kappa}{r}\right)G_{E\kappa J}(r) \;= \frac{1}{\hbar c}\left(E^{NR}+2mc^2-V(r)\right)F_{E\kappa J}(r)$$

$$\left(\frac{d}{dr}-\frac{\kappa}{r}\right)F_{E\kappa J}(r) \;= -\frac{1}{\hbar c}\left(E^{NR}-V(r)\right)G_{E\kappa J}(r)$$

Coupled radial equations: $E^{NR} \equiv E - mc^2$

$$\left(\frac{d}{dr}+\frac{\kappa}{r}\right)G_{E\kappa J}(r) \;=\frac{1}{\hbar c}\left(E^{NR}+2mc^2-V(r)\right)F_{E\kappa J}(r)$$

$$\left(\frac{d}{dr}-\frac{\kappa}{r}\right)F_{E\kappa J}(r) \;=-\frac{1}{\hbar c}\left(E^{NR}-V(r)\right)G_{E\kappa J}(r)$$

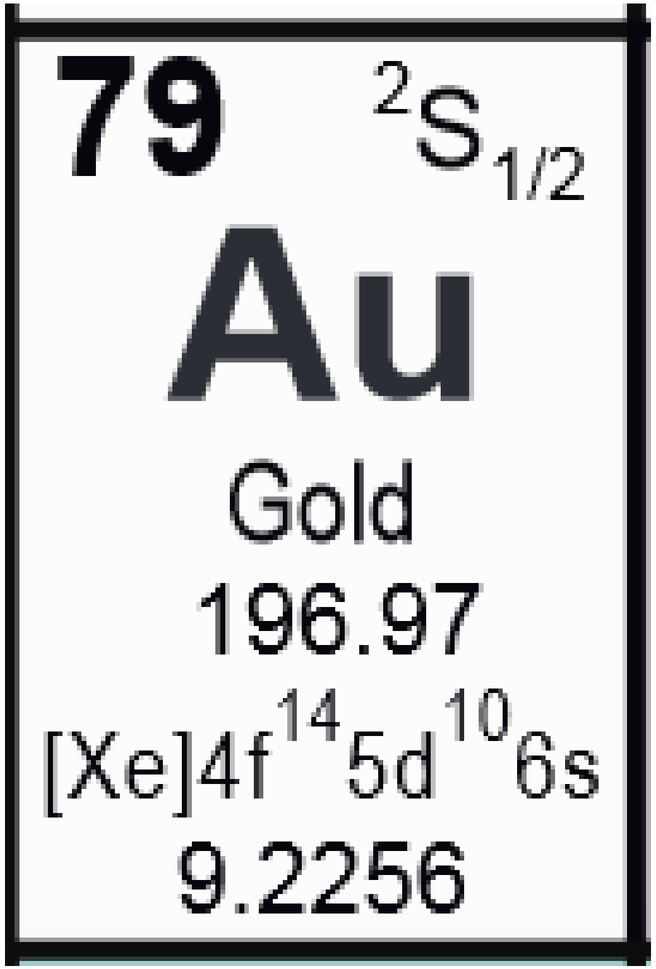
Normalization:

$$\int_0^\infty dr\left(G_{E\kappa J}^2(r)+F_{E\kappa J}^2(r)\right)=1$$

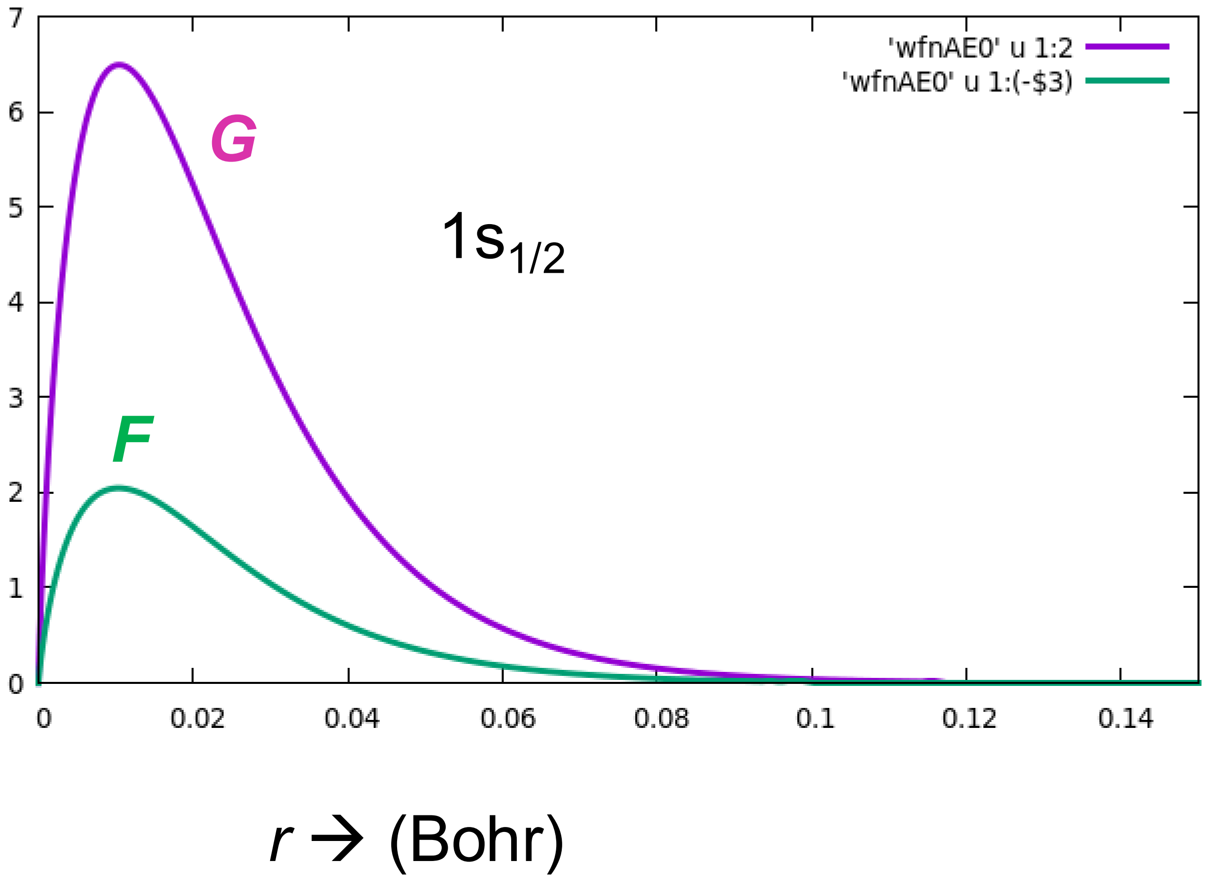
Note that eigenstates of J^2 have a degeneracy of $2J+1=2|\kappa|$

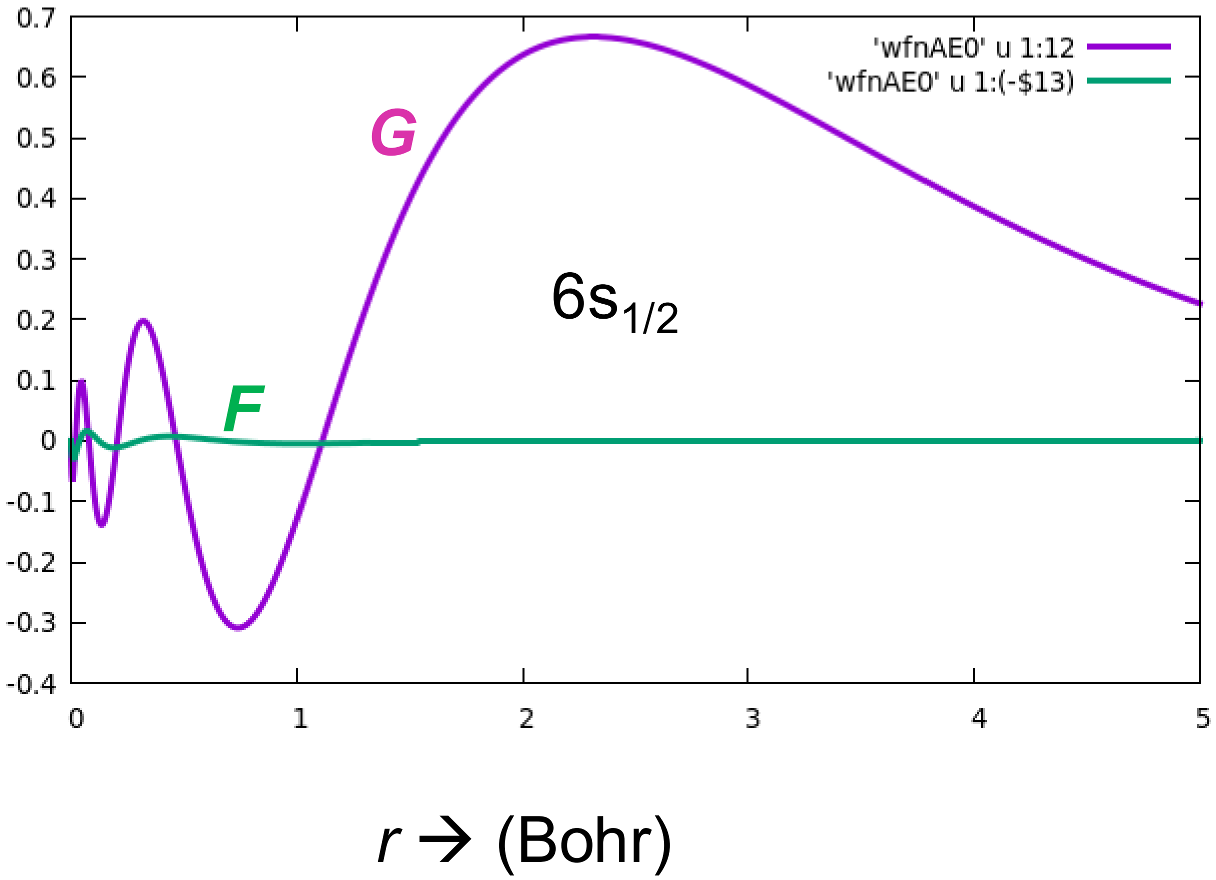
Numerical results for Au

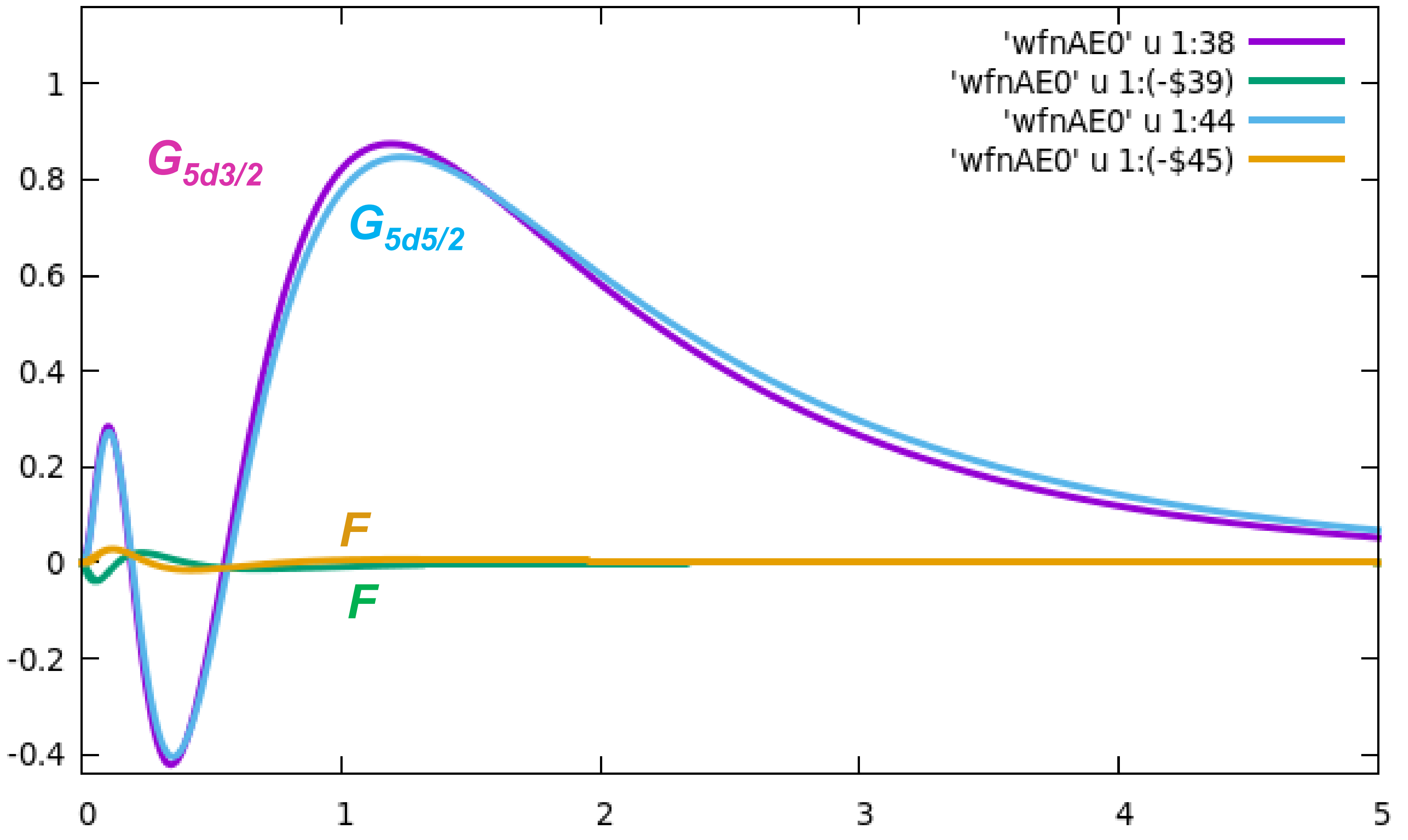
n	κ	l	occupancy	E (Ry)	
1	-1	0	2.0000000E+00	-5.9233999E+03	$1s_{1/2}$
2	-1	0	2.0000000E+00	-1.0443790E+03	$2s_{1/2}$
3	-1	0	2.0000000E+00	-2.4644922E+02	$3s_{1/2}$
4	-1	0	2.0000000E+00	-5.3440459E+01	$4s_{1/2}$
5	-1	0	2.0000000E+00	-7.9755620E+00	$5s_{1/2}$
6	-1	0	1.0000000E+00	-4.4827053E-01	$6s_{1/2}$
2	1	1	2.0000000E+00	-1.0016794E+03	$2p_{1/2}$
3	1	1	2.0000000E+00	-2.2723354E+02	$3p_{1/2}$
4	1	1	2.0000000E+00	-4.5251384E+01	$4p_{1/2}$
5	1	1	2.0000000E+00	-5.3102330E+00	$5p_{1/2}$
6	1	1	0.0000000E+00	-9.7322631E-02	$6p_{1/2}$
2	-2	1	4.0000000E+00	-8.6688708E+02	$2p_{3/2}$
3	-2	1	4.0000000E+00	-1.9749529E+02	$3p_{3/2}$
4	-2	1	4.0000000E+00	-3.8101322E+01	$4p_{3/2}$
5	-2	1	4.0000000E+00	-4.0844245E+00	$5p_{3/2}$
6	-2	1	0.0000000E+00	-5.5597043E-02	$6p_{3/2}$
3	2	2	4.0000000E+00	-1.6552601E+02	$3d_{3/2}$
4	2	2	4.0000000E+00	-2.4688226E+01	$4d_{3/2}$
5	2	2	4.0000000E+00	-5.9413837E-01	$5d_{3/2}$
3	-3	2	6.0000000E+00	-1.5913045E+02	$3d_{5/2}$
4	-3	2	6.0000000E+00	-2.3356823E+01	$4d_{5/2}$
5	-3	2	6.0000000E+00	-4.8110442E-01	$5d_{5/2}$
4	3	3	6.0000000E+00	-6.1354099E+00	$4f_{5/2}$
4	-4	3	8.0000000E+00	-5.8549892E+00	$4f_{7/2}$

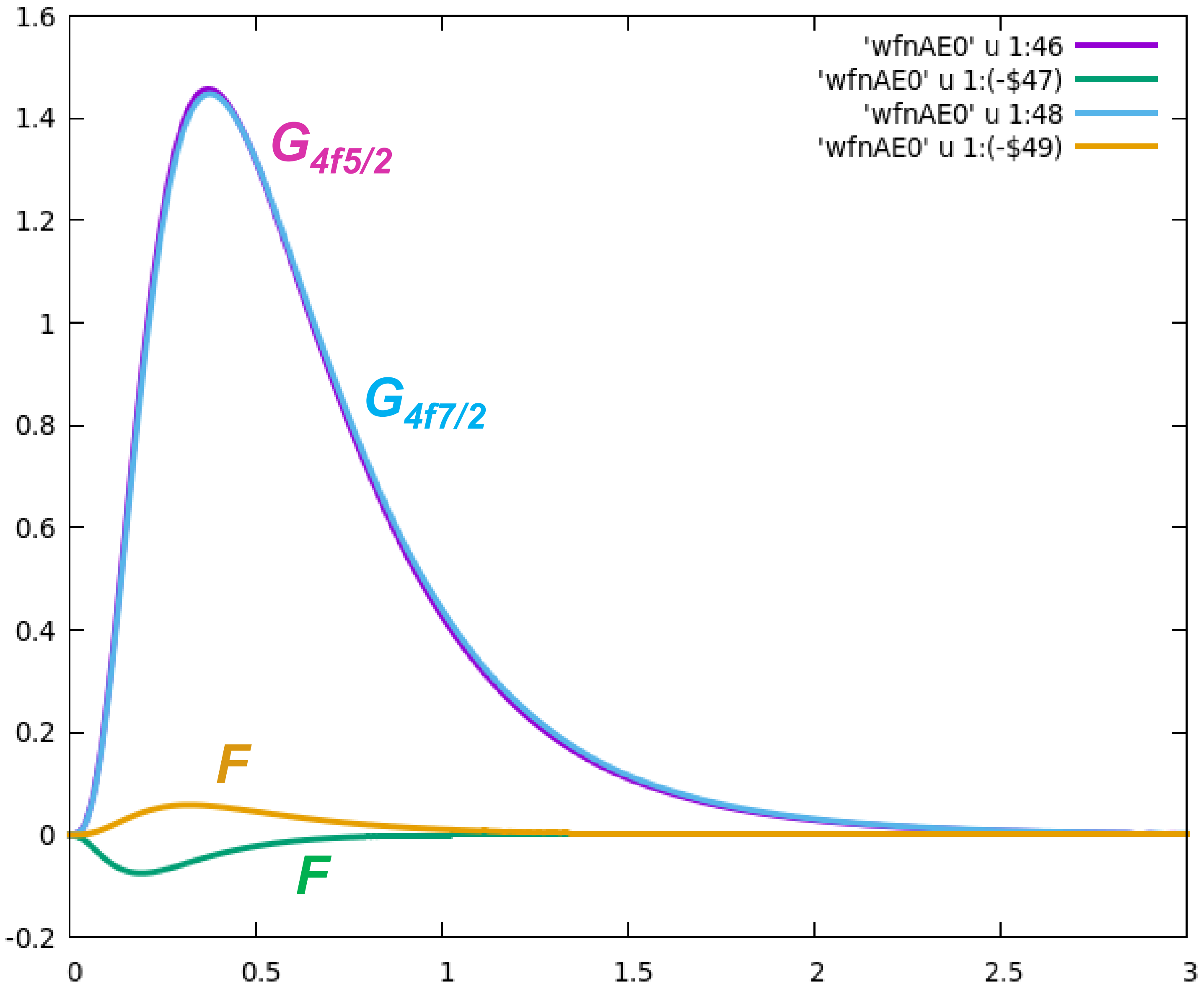


Radial wavefunctions for Au






'wfnAE0' u 1:38
'wfnAE0' u 1:(-$39)
'wfnAE0' u 1:44
'wfnAE0' u 1:(-$45)
$G_{5d3/2}$
$G_{5d5/2}$
F
F
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
0
1
2
3
4
5


'wfnAE0' u 1:46
'wfnAE0' u 1:(-$47)
'wfnAE0' u 1:48
'wfnAE0' u 1:(-$49)
$G_{4f5/2}$
$G_{4f7/2}$
F
F
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
0
0.5
1
1.5
2
2.5
3

More general treatment of bound states of Fermi particle within spherical potential $V(r)$ – continued

Some sample results within density functional theory
Ref. https://www.nist.gov/pml/data/results

Neon

10 Ne [He] $2s^2\,2p^6$

Energy unit is "Hartree
1H= 27.21138602 eV

	Non-relativistic	Relativistic	
1s	-30.305855	-30.314393	J=1/2
2s	-1.322809	-1.326075	J=1/2
2p	-0.498034	-0.500040	J=1/2
		-0.496232	J=3/2

Krypton

36 Kr [Ar] $3d^{10}$ $4s^2$ $4p^6$

	Non-relativistic	Relativistic	
1s	-509.982989	-517.456410	J=1/2
2s	-66.285953	-68.209637	J=1/2
2p	-60.017328	-61.753188 -59.789712	J=1/2 J=3/2
3s	-9.315192	-9.639319	J=1/2
3p	-7.086634	-7.347319 -7.057577	J=1/2 J=3/2
3d	-3.074109	-3.032140 -2.984281	J=3/2 J=5/2
4s	-0.820574	-0.851373	J=1/2
4p	-0.346340	-0.361325 -0.33742	J=1/2 J=3/2

Comments on approximate relativistic effects returning to free particle equations --

$$\left(i\hbar\frac{\partial}{\partial t}-\mathbf{p}\cdot\boldsymbol{\sigma}c\right)\left(i\hbar\frac{\partial}{\partial t}+\mathbf{p}\cdot\boldsymbol{\sigma}c\right)\Psi=\left(mc^2\right)^2\Psi$$

Assume harmonic time dependence -- $\Psi(\mathbf{r},t)\Rightarrow\Psi(\mathbf{r})e^{-iEt/\hbar}$

Also add scalar potential central $V(r)$

$$\left(E-V(r)-\mathbf{p}\cdot\boldsymbol{\sigma}c\right)\left(E-V(r)+\mathbf{p}\cdot\boldsymbol{\sigma}c\right)\Psi=\left(mc^2\right)^2\Psi$$

Noting that the non-relativistic energy is $E^{NR}=E-mc^2$

we can keep the largest terms:

$$\left(\frac{\mathbf{p}^2}{2m}+V(r)-\frac{\mathbf{p}^4}{8m^3c^2}+\underbrace{\frac{\hbar}{4m^2c^2}\frac{1}{r}\frac{dV}{dr}\boldsymbol{\sigma}\cdot\mathbf{L}}_{\text{Spin-orbit}}-\underbrace{\frac{\hbar^2}{8m^2c^2}\nabla^2V}_{\text{Darwin term}}\right)\Psi=E^{NR}\Psi$$