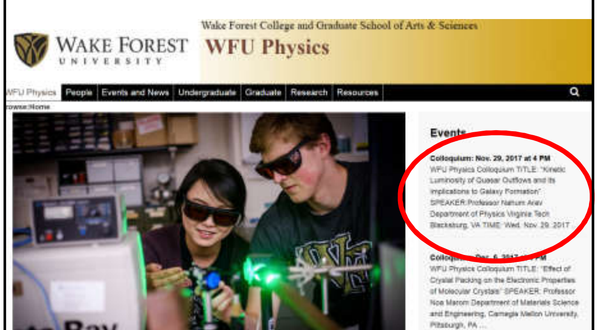
PHY 741 Quantum Mechanics
12-12:50 AM MWF Olin 103

Plan for Lecture 35:

Chap. 20 in Shankar – Supplemented with J. J. Sakurai -- Dirac equation for hydrogen-like ions and other atoms

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

22	Mon, 10/23/2017	Chap. 15	Multi-electron atoms	#13	10/25/2017
23	Wed, 10/25/2017	Chap. 15	Multi-electron atoms	#14	10/30/2017
24	Fri, 10/27/2017		Effects of nuclear motion		
25	Mon, 10/30/2017	Chap. 17	Time-independent perturbation theory	#15	11/3/2017
26	Wed, 11/01/2017	Chap. 17	Time-independent perturbation theory		
27	Fri, 11/03/2017		Effects of a static magnetic field		
28	Mon, 11/06/2017	Chap. 18	Time-dependent perturbation theory	#16	11/10/2017
29	Wed, 11/08/2017	Chap. 18	Time-dependent perturbation theory		
30	Fri, 11/10/2017	Chap. 19	Scattering theory	#17	11/15/2017
	Mon, 11/13/2017		*Class cancelled*		
31	Wed, 11/15/2017	Chap. 19	Scattering theory		
32	Fri, 11/17/2017	Chap. 20	Dirac Equation		
33	Mon, 11/20/2017	Chap. 20	Dirac Equation		
	Wed, 11/22/2017		*Thanksgiving Holiday -- No class*		
	Fri, 11/24/2017		*Thanksgiving Holiday -- No class*		
34	Mon, 11/27/2017	Chap. 20	Dirac Equation		
35	Wed, 11/29/2017	Chap. 20	Dirac Equation		
36	Fri, 12/01/2017	Chap. 1-20	Review		
	Mon, 12/04/2017		Presentations I		
	Wed, 12/06/2017		Presentations II		
	Fri, 12/08/2017		Presentations III		



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

$$H = \mathbf{p}\cdot\boldsymbol{\alpha}c + mc^2\beta + V(\mathbf{r})I_4$$

For H-like ion with nuclear charge Z:

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

$$i\hbar\frac{\partial}{\partial t}\Psi = H\Psi$$

Stationary state solutions:

$$\Psi(\mathbf{r},t) = \begin{pmatrix}\varphi^U(\mathbf{r})\\ \varphi^L(\mathbf{r})\end{pmatrix} e^{-iEt/\hbar}$$

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

Exact solution of Dirac equation for H-like ion:

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

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

Fine-structure constant:

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

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

Comparison with Schroedinger equation --

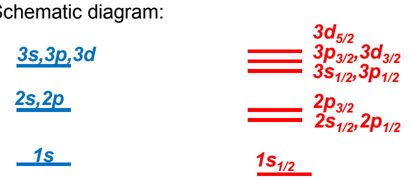
Schroedinger equation

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

Dirac equation

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

Schematic diagram:



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

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

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

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

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

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

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

Eigenvalue problem:

$$H\begin{pmatrix} g_{E\kappa J}(r)\chi_{\kappa JM}(\hat{\mathbf{r}}) \\ if_{E\kappa J}(r)\chi_{-\kappa JM}(\hat{\mathbf{r}})\end{pmatrix} = E\begin{pmatrix} g_{E\kappa J}(r)\chi_{\kappa JM}(\hat{\mathbf{r}}) \\ if_{E\kappa J}(r)\chi_{-\kappa JM}(\hat{\mathbf{r}})\end{pmatrix}$$

Coupled differential equations for radial functions:

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

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

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

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

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

Note that for an electron, $mc^2=0.511\times10^6$ 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:

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

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

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:

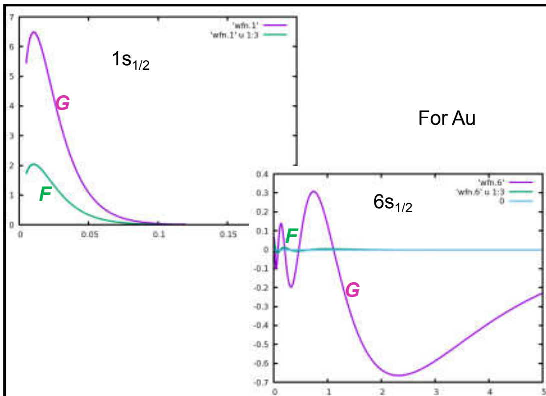
$$\int_0^\infty dr\left(G_{E\kappa J}^2(r)+F_{E\kappa J}^2(r)\right)=1$$

Example results for Au (from an old code)

(Ry units)

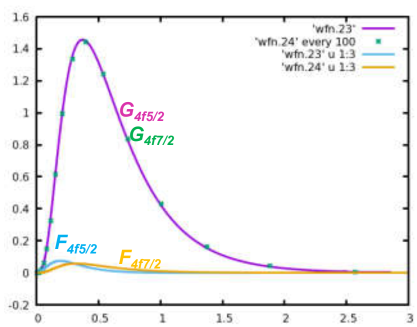
orbital	n	l	j	electrons	eigenvalue
1s1/2	1.0	0.0	0.5	2.00000	-0.5885793E+04
2s1/2	2.0	0.0	0.5	2.00000	-0.1038877E+04
3s1/2	3.0	0.0	0.5	2.00000	-0.2452955E+03
4s1/2	4.0	0.0	0.5	2.00000	-0.5317353E+02
5s1/2	5.0	0.0	0.5	2.00000	-0.7924445E+01
6s1/2	6.0	0.0	0.5	1.00000	-0.4418839E+00
2p1/2	2.0	1.0	0.5	2.00000	-0.9968347E+03
2p3/2	2.0	1.0	1.5	4.00000	-0.8637198E+03
3p1/2	3.0	1.0	0.5	2.00000	-0.2262938E+03
3p3/2	3.0	1.0	1.5	4.00000	-0.1968880E+03
4p1/2	4.0	1.0	0.5	2.00000	-0.4505248E+02
4p3/2	4.0	1.0	1.5	4.00000	-0.3797896E+02
5p1/2	5.0	1.0	0.5	2.00000	-0.5276965E+01
5p3/2	5.0	1.0	1.5	4.00000	-0.4064096E+01
6p1/2	6.0	1.0	0.5	0.00000	-0.9497264E-01
6p3/2	6.0	1.0	1.5	0.00000	-0.5468687E-01
3d3/2	3.0	2.0	1.5	4.00000	-0.1652289E+03
3d5/2	3.0	2.0	2.5	6.00000	-0.1588723E+03
4d3/2	4.0	2.0	1.5	4.00000	-0.2464986E+02
4d5/2	4.0	2.0	2.5	6.00000	-0.2332576E+02
5d3/2	5.0	2.0	1.5	4.00000	-0.5890101E+00
5d5/2	5.0	2.0	2.5	6.00000	-0.4765816E+00
4f5/2	4.0	3.0	2.5	6.00000	-0.6152851E+01
4f7/2	4.0	3.0	3.5	8.00000	-0.5872657E+01

nuclear charge= 79.000000



For Au

For Au



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

https://www.nist.gov/pml/atomic-reference-data-electronic-structure-calculations-trends-across-periodic-table

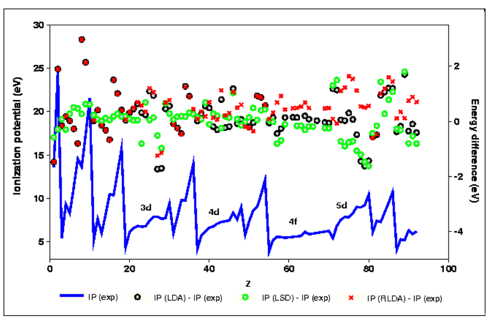


Fig. 9: Ionization potentials of the elements, as obtained from experiment (blue line, to be referred to scale on left)); and differences of calculated and experimental values for the LDA (black), LSD (green), and RLDA (red) approximations, all to be referenced to the right-hand energy scale.