PHY 742 Quantum Mechanics
1:00-1:50 AM MWF Olin 103

Plan for Lecture 17:
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**

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10	Wed: 02/05/2020	Chap. 2,6	H_2^+ molecular ion; Born Oppenheimer approximation	#10	02/12/2020
11	Fri: 02/07/2020	Chap. 15	Time-dependent perturbations	#11	02/14/2020
12	Mon: 02/10/2020	Chap. 15	Time-dependent perturbations	#12	02/14/2020
13	Wed: 02/12/2020	Chap. 15	Time-dependent perturbations	#13	02/17/2020
14	Fri: 02/14/2020	Chap. 16	The Dirac equation		
15	Mon: 02/17/2020	Chap. 16	The Dirac equation	#14	02/19/2020
16	Wed: 02/19/2020	Chap. 16	The Dirac equation	#15	02/21/2020
17	Fri: 02/21/2020	Chap. 16	The Dirac equation	#16	02/24/2020
18	Mon: 02/24/2020				
19	Wed: 02/26/2020				
20	Fri: 02/28/2020				
	Mon: 03/02/2020	No class	*APS March Meeting*	Take Home Exam	
	Wed: 03/04/2020	No class	*APS March Meeting*	Take Home Exam	
	Fri: 03/06/2020	No class	*APS March Meeting*	Take Home Exam	
	Mon: 03/09/2020	No class	*Spring Break*		
	Wed: 03/11/2020	No class	*Spring Break*		
	Fri: 03/13/2020	No class	*Spring Break*		
21	Mon: 03/16/2020				
22	Wed: 03/18/2020				

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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: $|JM\rangle$

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

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

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

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

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Coupled differential equations for radial functions:

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

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

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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

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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

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

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

Comparison with Schrödinger equation --

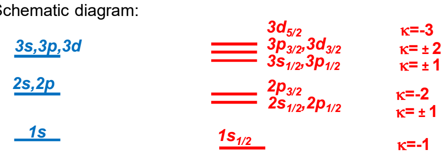
Schrödinger equation

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

Dirac equation

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

Schematic diagram:



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

Dirac equation

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

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

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

$\Rightarrow$ 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.

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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:

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

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Some details

Exact solution of Dirac equation for H-like ion:

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

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

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

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

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

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

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

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

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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 $f_{E\kappa J}(r)=F_{E\kappa J}(r)/r$

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

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

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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:

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

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

Approximate radial equation for upper component

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

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

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

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

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

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

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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:

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

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Example results for Au (from an old code)

orbital	n	l	j	electrons	eigenvalue (Ry units)
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

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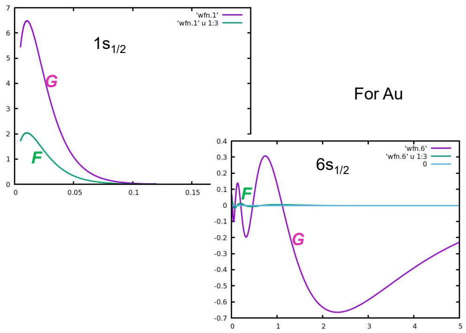

For Au

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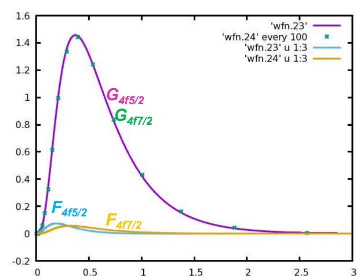
For Au



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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

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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

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