Lecture 9
Dirac-Hartree-Fock code. Second-order perturbation theory and running second-order code. Atomic calculations and the search for the variation of the fine-structure constant.

Dirac-Hartree-Fock code (DHF). To run the code: ./dhf <na.in

Walter Johnson, "Atomic structure theory"

This is a relativistic code, so the input labels states by principal quantum number n and relativistic quantum number κ. The advantage of relativistic quantum number κ is that it specifies both angular quantum number and total angular quantum number for the electron.

Relativistic quantum number $\kappa = \mp(j + \frac{1}{2})$ for $j = \ell \pm \frac{1}{2}$

Its values for a few first states are:

state(ℓj)	κ
s	-1
$p_{1/2}$	1
$p_{3/2}$	-2
$d_{3/2}$	2
$d_{5/2}$	-3

Input for the DHF code

Do not change the input that is crossed out below

```
Na    9   11   23    0    0   11    5    1
 1   -1    0
 2   -1    0
 2    1    0
 2   -2    0
 3   -1    1         -0.1
 3    1    1         -0.1
 3   -2    1         -0.1
 3    2    1         -0.05
 3   -3    1         -0.05
1.5
 0.00   0.0000   500
 1
 0.00000 2.8853 2.30000
 0
```

```
Na    9   11   23   0̸   0̸   1̸1̸    5   1̸
 1   -1    0
 2   -1    0
 2    1    0
 2   -2    0
 3   -1    1         -0.1
 3    1    1         -0.1
 3   -2    1         -0.1
 3    2    1         -0.05
 3   -3    1         -0.05
1̶.5̶
 0̶.̶0̶0̶   0̶.̶0̶0̶0̶0̶   5̶0̶0̶
 1̶
 0̶.̶0̶0̶0̶0̶0̶ 2.8853 2̶.̶3̶0̶0̶0̶0̶
 0̶
```

Line 1

Top section

4+1

4 "core" shells

```
         Na   9   11   23   0   0   11   5   1
          1  -1   0
          2  -1   0
          2   1   0
          2  -2   0
          3  -1   1        -0.1
          3   1   1        -0.1
          3  -2   1        -0.1
          3   2   1        -0.05
          3  -3   1        -0.05
        1.5
          0.00   0.0000   500
            1
          0.00000 2.8853 2.30000
            0
```

9 lines total

first valence line input

$1s^2 2s^2 2p^2_{1/2} 2p^4_{3/2}$ "Core" for Na

3s is the ground state
3p, 3d are excited states

Middle section

```
              Na    9   11   23   0   0   11   5   1
         1s    1  -1   0
   core  2s    2  -1   0       0 for
electrons 2p1/2 2   1   0       core
         2p3/2 2  -2   0
         3s    3  -1   1         -0.1
valence  3p1/2 3   1   1   for   -0.1
electrons 3p3/2 3  -2   1  valence -0.1
(can add  3d3/2 3   2   1         -0.05
excited   3d5/2 3  -3   1         -0.05
states)      1.5
           0.00   0.0000   500
             1
           0.00000 2.8853 2.30000
             0
```

1 for valence

← initial energy guesses in a.u. You can keep these the same for alkali-metals.

Grid line note

```
0.00   0.0000   500
```
← This line tells the code to use default radial grid. Do not change.

Bottom section

```
  1
    0.00000 2.8853 2.30000
```

This part defines the nuclear charge distribution to be the Fermi distribution and gives its parameters:

$$\rho(r) = \frac{\rho_0}{1 + \exp\left(\frac{r-c}{a}\right)}$$

Parameter c is the 50% radius (I will provide the numbers).
Parameter t=a(4ln3) can be taken 2.3 for all cases.
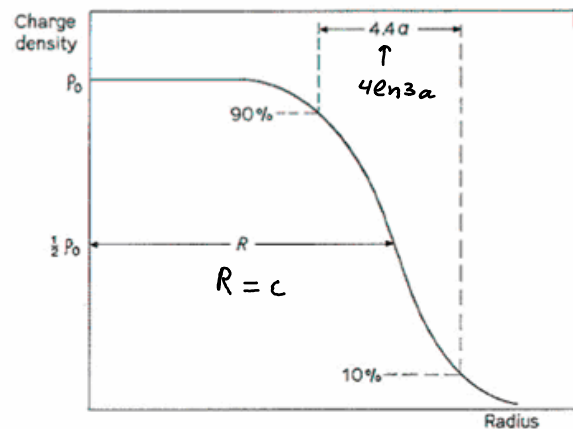
OUTPUT:

```
        Dirac Hartree Fock Levels for    Na

   shell      m    atomic units         breit              qed              f.s.

   1s       293     -40.826546376      0.0187383        0.0064254        0.0000297
   2s       337      -3.082400565      0.0011619        0.0002717        0.0000018
   2p*      345      -1.801417667      0.0014418       -0.0000029        0.0000000
   2p       345      -1.794009083      0.0010118        0.0000031        0.0000000
   3s       377      -0.182032692      0.0000263        0.0000028        0.0000000
   3p*      387      -0.109490451      0.0000127       -0.0000000        0.0000000
   3p       387      -0.109416519      0.0000088        0.0000000        0.0000000
   3d*      399      -0.055666595      0.0000001       -0.0000000        0.0000000
   3d       399      -0.055666801      0.0000000       -0.0000000        0.0000000


       etotal:    -161.8959046       0.0233656        0.0134005


   with val :     -162.0779373       0.0233919        0.0134033
 inuc =   4   rnuc = 2.9630fm   rnuc =    0.000056
```

You only need the part that gives valence energies in atomic units. The code designates $j=\ell-1/2$ states with *, i.e. 3p*=$3p_{1/2}$ and 3p=$3p_{3/2}$. We first convert the results into cm^{-1} using 1 a.u. (energy) = 219474.6314 cm^{-1} and then subtract out the 3s energy (ground state) since NIST database gives the energies relative to the ground state. We are ready to compare with experimental data. Go to

NIST atomic spectra database (need "LEVELS")
http://www.nist.gov/pml/data/asd.cfm

and type in "Na I". To copy the data, ASCII table might be easier than HTML. The results of our comparison are:

Configuration	DHF (a.u.)	DHF (cm^{-1})	Energy-E(3s)	Experiment	Diff.(%)
3s	-0.182033	-39952	0	0	
$3p_{1/2}$	-0.109490	-24030	15921	16956	6.1%
$3p_{3/2}$	-0.109417	-24014	15937	16973	6.1%
$3d_{3/2}$	-0.055667	-12217	27734	29173	4.9%
$3d_{5/2}$	-0.055667	-12217	27734	29173	4.9%

As you can see, the agreement is pretty good, 5-6%!

To compare the 3s energy scroll down the NIST table until you get to the ionization limit (Na II). This line looks like:

Na II (2p6 1S<0>) | Limit | --- | 41449.451(2)

Note that this is not necessarily the last line in the table!
This is your 3s removal energy (so it is listed with + sign). The difference between our value of 39952cm^{-1} and experiment 41449.451(2)cm^{-1} is only 3.6%!

We can also compare the fine-structure splittings for 3p states with experiment. To do so, subtract the $3p_{3/2}$ and $3p_{1/2}$ energies. DHF code gives 16.2 cm^{-1} while the experimental result is 17.2 cm^{-1}, i.e. 5.6% difference.

Note that the fine-structure splitting for 3d is very small, 0.05cm^{-1}. Note that the fine-structure is inverted.

To improve these results, we will use the second-order perturbation theory.
As a very quick review, we give a summary of the main results for the non-degenerate perturbation theory from the Quantum Mechanics II (425) course.

Non-degenerate perturbation theory: summary

The problem of the perturbation theory is to find eigenvalues and eigenfunctions of the perturbed potential, i.e. to solve approximately the following equation:

$$H \psi_n = E \psi_n \quad , \quad H = H^0 + H'$$

$$\uparrow \text{perturbation}$$

using the known solutions of the problem

$$H^0 \psi_n^0 = E_n^0 \psi_n^0 .$$

$$\psi_n = \psi_n^0 + \psi_n^1 + \psi_n^2 + \dots$$

$$E_n = E_n^0 + E_n^1 + E_n^2 + \dots$$

The first-order energy is given by:

$$\boxed{E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle} \qquad (1)$$

First-order correction to the wave function is given by ;

$$\boxed{\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \psi_m^0} \qquad (2)$$

The second-order correction to the energy is

$$E_n^2 = \sum_{m \neq n} \frac{\langle \psi_n^0 | H' | \psi_m^0 \rangle \langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \qquad (3)$$

The main feature of the second-order formula is the sum involving summation over ALL POSSIBLE states of the atom, including the continuum spectrum. The numerical implementation of such sums involves creation of a finite basis set of the atomic wave functions. Practically, such basis set may be created by "placing" atom is a spherical box. Then, the summation is reduced to a (finite) sum over all basis set states, which is equivalent to summing over all "real" states and integration over the continuum.

The code BASIS will generate a finite basis set constrained to a spherical cavity on a nonlinear grid using B-splines. First run ./DHF <na.in to make DHF potential and then run ./BASIS <spl.in to produce the corresponding finite basis set for the subsequent second-order calculations. Then, you can run second-order energy code ./E2 <nae2.in .

What about first order? In the case of the DHF "frozen-core" starting potential, one can show that the first order is zero.

Running of the second-order code for Na

1) Run ./DHF <na.in and ./BASIS <spl.in (do not change spl.in for any homework cases)
2) Run ./E2 <nae2.in

Second-order input (also uses n κ labels of configurations just as DHF does.)
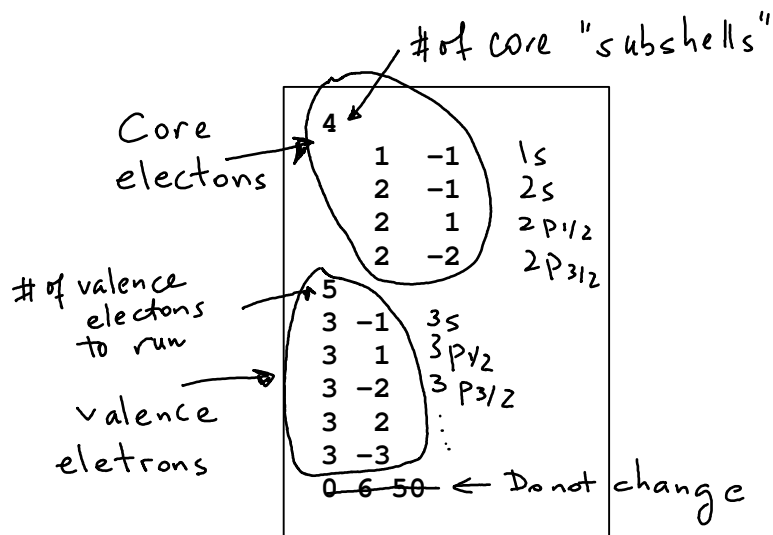
Output gives the state and its second-order energy:

```
3    -1  -0.005853626
3     1  -0.001775692
3    -2  -0.001767014
3     2  -0.000225822
3    -3  -0.000225818
```

These values have to be added to DHF values to obtain the total results. Let's compare the DHF+E2 results with experiment:

Configuration	DHF (a.u.)	E2 (a.u.)	Total (a.u)	Total (cm^{-1})	Energy-E(3s)	Expt.	Diff.(%)
3s	-0.182033	-0.005854	-0.187886	-41236	0	0	
$3p_{1/2}$	-0.109490	-0.001776	-0.111266	-24420	16816	16956	0.83%
$3p_{3/2}$	-0.109417	-0.001767	-0.111184	-24402	16834	16973	0.82%
$3d_{3/2}$	-0.055667	-0.000226	-0.055892	-12267	28969	29173	0.70%
$3d_{5/2}$	-0.055667	-0.000226	-0.055893	-12267	28969	29173	0.70%

Much better results!!! The second-order result for the ionization potential 41236 cm^{-1} is also in much better agreement with experiment, 41449.45cm^{-1}, 0.5%.

Atomic calculations and search for the variation of the fine-structure constant $\alpha = \dfrac{e^2}{4\pi\epsilon_0}\dfrac{1}{\hbar c}$

The modern theories directed toward unifying gravitation with the three other fundamental interactions suggest variation of the fundamental constants in an expanding universe. Controversial studies of the quasar absorption spectra indicate that the fine-structure constant may have been different in a distant past. This result has not been confirmed by other groups using a different telescope and the status of the observational search for α-variation is presently unclear and further investigations are required.

Development of ultra-precise atomic clocks allowed laboratory tests of the α-variation at the present time. Different optical atomic clocks use transitions that have different contributions of the relativistic corrections to frequencies. Therefore, comparison of these clocks can be used to search for α-variation. Certain atomic systems exhibit much higher sensitivity to the variation of α. The sensitivity of atomic transitions to α-variation for both astrophysics and laboratory searches is determined from theoretical calculations such as demonstrated below.

The sensitivity of the atomic transition frequency ω to the variation of the fine-structure constant α can be quantified using a coefficient q defined as

$$\omega(x) = \omega_0 + qx, \qquad x = \left(\frac{\alpha}{\alpha_0}\right)^2 - 1$$

The frequency ω_0 corresponds to the value of the fine-structure constant α_0 at some initial point in time. In the experiment, ratio of two frequencies, which is a dimensionless quantity, is studied over time. Therefore, it is preferable to select transitions with significantly different values of q. We note that q may be either positive or negative. It is convenient to also define dimensionless enhancement factor K=2q/ω.

To calculate the value of the sensitivity coefficient q, we carry out three calculations with different values of α. In the first calculation, current CODATA value is used. In the other two calculations, the value α^2 is varied by ±5%. The value of q is then determined as a numerical derivative

$$q = \frac{\omega(0.05) - \omega(-0.05)}{0.1}$$

Let's carry out such calculation for Na states that we have calculated in the previous example.

The version of the DHF code that allow varying the constant α is called DHFa. Its input is the same as in the DHF with the exception on the last line that gives the change in α^2.

```
Na  9 11 23  0  0 11  5  1
 1 -1  0
 2 -1  0
 2  1  0
 2 -2  0
 3 -1  1    -0.1
 3  1  1    -0.1
 3 -2  1    -0.1
 3  2  1    -0.05
 3 -3  1    -0.05
1.5
 0.00 0.0000 500
 1
 0.00000 2.8853 2.30000
 0
0.95
```

To change α^2 by − 5%

The results of Na calculation are summarized in the table below.

Configuration	DHF (cm-1)	DHF ($\alpha^2 = 0.95\alpha^2_0$)	DHF ($\alpha^2 = 1.05\alpha^2_0$)	q	K=2q/ω
3s	0	0	0	0	0
$3p_{1/2}$	15921	15919	15923	39	0.005
$3p_{3/2}$	15937	15935	15940	56	0.007
$3d_{3/2}$	27734	27732	27737	51	0.004
$3d_{5/2}$	27734	27732	27737	51	0.004

As you can see, even such large variation of α^2 as 5% produces a very small effect on the transition energies in Na, ~2cm^{-1}.

The α-variation effects are significantly enhanced in heavy systems. Here are the results of the same calculation for Fr:

Configuration	DHF (cm⁻¹)	DHF ($\alpha^2=0.95\alpha^2_0$)	DHF ($\alpha^2=1.05\alpha^2_0$)	q	K=2q/ω
7s	0	0	0	0	0
7p$_{1/2}$	9912	9757	10077	3195	0.645
7p$_{3/2}$	11112	10876	11361	4850	0.873
6d$_{3/2}$	14942	14660	15235	5758	0.771
6d$_{5/2}$	14843	14571	15126	5555	0.748

The sensitivity to α-variation is 80 times larger than for a similar ns-np$_{1/2}$ transition in Na! This is why the most accurate laboratory study was conducted for Al+/Hg+ clocks: Al+ is not very sensitive to α-variation while heavy Hg+ has a very large enhancement.

Here is an example of the systems (highly-charged ions) which are very sensitive to α-variation:

TABLE III: Energies and sensitivity coefficients q for Ag-like ions relative to the ground state evaluated in the SDpT all-order approximation in cm^{-1}; $K = 2q/\omega$ is the enhancement factor. Lowest-order DF sensitivity coefficients q are given for comparison.

Ion	Level	Energy	q (DF)	q (SDpT)	K
Nd^{13+}	$5s_{1/2}$	0	0	0	
	$4f_{5/2}$	55706	102609	104229	3.7
	$4f_{7/2}$	60134	106276	108243	3.6
	$5p_{1/2}$	185028	16047	15953	0.2
	$5p_{3/2}$	234887	71013	72079	0.6
Sm^{15+}	$4f_{5/2}$	0	0	0	
	$4f_{7/2}$	6444	5536	5910	1.8
	$5s_{1/2}$	60517	-132449	-134148	-4.4
	$5p_{1/2}$	268604	-113153	-114999	-0.9
	$5p_{3/2}$	333385	-40883	-41477	-0.2