MCDF Calculations on Pm-like Ions in an Isoelectronical Sequence

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Abstract

Calculations on Pm I like ions in a isoelectronical sequence has been made using Multiconfigurational Dirac-Fock (MCDF). Spectra in these heavy atoms are very massive and complicated as so many shells are open and so many transitions are possible. Moving down the ion sequence the electron configuration is going to change due to increasing nuclear charge. The work was focused on finding when a configuration giving a simple spectrum is the lowest lying energy level. All calculations were made using GRASP (General Relativistic Atomic Structure Package).

Contents

1   Theory

1.1   The Hamiltonian

In quantum mechanics an atom can be fully described from its wave function ψ. Using the schrödinger equation (SE)

$$H\Psi = E\Psi \tag{1}$$

the energy of the system can obtained where the non relativistic hamiltonian H is

$$H = -\frac{h^2}{2m}\nabla^2 + V(r) \tag{2}$$

for a one electron system. As we are dealing with heavy ions with large nuclear mass and several electrons we need to use a relativistic hamiltonian with interactions between the electrons. The Dirac-Coulomb Hamiltonian is written as

$$H_{DC} = \sum_{i=1}^{N}\left(\alpha_i \cdot p_i c + (\beta_i - 1)c^2 - \frac{Z}{r_i}\right) + \sum_{i>j}^{N}\frac{1}{r_{ij}} \tag{3}$$

where α and β

$$\alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix} \tag{4}$$

$$\beta = \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix} \tag{5}$$

where σ is the Pauli spin matrices and I and 0 are the unit respectively zero matrices. As it is known many-body problems are not easy to solve and the electron-electron interactions, the $\frac{1}{r_{ij}}$ term in Eq(3), becomes impossible to solve exactly or explicitly for the ions in these calculations. As such some approximations is needed to simplify the system to a level where it's possible to solve the SE for the system.

1.2   Central Field Approximation

The first approximation made is the central field approximation where the hamiltonian is split up

$$H_{DC} = H_0 + V(r) \tag{6}$$

where V(r) is

$$V(r) = \sum_{i>j}^{N}\frac{1}{r_{ij}} - \sum_{i=1}^{N}U(r_i) + \frac{Z}{r_i} \tag{7}$$

The electrons are treated as moving in a consistent field created by all the electrons and the H_{DC} is reduced to a single body problem.

1.3 State functions

We can separate H_0 into one electron equations H_i as

$$H_i \psi_\alpha(F_i) = E_i \psi_\alpha(F_i) \tag{8}$$

where α is a specific electron state defined by a set of quantum numbers $\{n_\alpha \kappa_\alpha m_\alpha\}$ using κ to simplify equations to come as $\kappa = \pm(j + 1/2)$ The one electron equations can then be written as

$$\psi_{n\kappa}(r) = \frac{1}{r} \begin{pmatrix} P_{n\kappa}(r) & \chi_{\kappa m}(\theta, \phi) \\ iQ_{n\kappa}(r) & \chi_{-\kappa m}(\theta, \phi) \end{pmatrix} \tag{9}$$

where $P_{n\kappa}$ and $Q_{n\kappa}$ are the radial parts and χ-terms are the spin-orbit parts. Using Slater determinants we can construct the full N-electron system by taking the product of all the one-electron functions. By taking linear combinations of Slater determinants we can form states that are the simultaneous eigenfunctions of H_0, J^2, J_z and π. These state functions $\Phi(\alpha_j J)$ are called CSFs (Configuration State Functions) where α_j contains enough parameters to define each state uniquely.

Atomic state functions (ASFs) can now be defined by taking a linear combination of CSFs with the same J value as

$$\Psi(\gamma J) = \sum_j c_j \Phi(\alpha_j J) \tag{10}$$

where c_j are so called mixing coefficients and are obtained by diagonalizing the energy matrix with the requirement $\sum_j c_j^2 = 1$.

1.4 Multi Configurational Dirac Fock

Using linear combinations of CSFs the energy expression for the atom becomes

$$\epsilon(\gamma J) = \sum_{i=1}^{M} \sum_{j=1}^{M} c_i c_j \langle \Psi(\gamma_i J) | \mathcal{H} | \Psi(\gamma_j J) \rangle \tag{11}$$

$$= \sum_{i=1}^{M} c_i^2 H_{ii} + 2 \sum_{j=1}^{M} c_i c_j H_{ij} \tag{12}$$

with the hamiltonian matrix

$$H_{ij} = < \Phi(\gamma_i J) | \mathcal{H} | \Phi(\gamma_j J) > \tag{13}$$

Introducing $\mathbf{c} = (c_1, c_2, ..., c_M)^\dagger$ as a vector of the mixing coefficients the energy expression can be written as

$$E = \mathbf{c}^\dagger \mathbf{H} \mathbf{c} \tag{14}$$

The expression can be improved further with the use the theory of angular momenta we can replace the hamiltonian H_{ij} with

$$H_{ij} = \sum_{ab} \omega_{ab}^{ij} I(a, b) + \sum_{abcd} \sum_k v_{abcd;k}^{ij} R^k(ab, cd) \tag{15}$$

where the radial integral $I(a, b)$ and the Slater integral $R^k(abcd)$ as

$$I(a, b) = \int_0^\infty dr \left[cQ_a \left(\frac{d}{dr} + \frac{\kappa}{r} \right) P_b + cP_a \left(-\frac{d}{dr} + \frac{\kappa}{r} \right) Q_b - 2c^2 Q_a Q_b - \frac{Z}{r} (P_a P_b + Q_a Q_b) \right] \tag{16}$$

$$R^k(abcd) = \int_0^\infty \rho_{ac}^e(r) Y_k(bd; r) \frac{dr}{r} = \int_0^\infty \rho_{bd}^e(r) Y_k(ac; r) \frac{dr}{r} \tag{17}$$

where $\rho_{ab}^e(r)$ and $Y_k(ab; r)$ are

$$\rho_{ab}^e(r) = P_a(r) P_b(r) + Q_a(r) Q_b(r) \tag{18}$$

$$Y_k(ab; r) = r \int_0^\infty \frac{r_<^k}{r_>^{k+1}} \rho_{ab}^e(s) ds \tag{19}$$

By substituing (15) into (12) and using

$$\omega_{ab} = \sum_{i=1}^M \sum_{j=1}^M c_i c_j \omega_{ab}^{ij} \tag{20}$$

$$v_{abcd;k} = \sum_{i=1}^M \sum_{j=1}^M c_i c_j v_{abcd;k}^{ij} \tag{21}$$

the energy can be written as

$$\epsilon(\gamma J) = \sum_{ab} \omega_{ab} I(a, b) + \sum_{abcd;k} v_{abcd;k} R^k(ab, cd) \tag{22}$$

2 Methods of calculation

2.1 Self-Consistent Field

The calculations in the GRASP rely on EOL(Extended Optimal Level) calculations for optimization. By optimizing the weighted sum of the total energy with respect to the specific ASFs the self-consistent field procedure used will be

1. Obtain initial preset estimates of the wave functions.
2. Diagonalize the Hamiltionian matrix to obtain the mixing coefficients c.
3. Solve the MCDF equations using the mixing coefficients from step 2.
4. Step 2 and 3 is repeated until a specific convergence is reached.

2.2 Multiconfiguration setup

To start each calculation one must set up the Atomic state function to use for the specific case. Starting out with a single CSF for the state of interest and add more CSF of interest. By deciding what orbitals should be allowed and setting the number of electrons possible to occupy different orbitals all possible CSFs for the ASF can then be derived.
This multiconfiguration approach will improve the results as some of the correlations between different states with the same J will be handled.

2.3 Correlation effects

To determine what orbitals to include and how many electrons to excite from each subshell it is important to determine what needs to be included. Depending on the possible setups available different correlations will be accounted for. Having two valance electrons in the outermost orbital with a closed core will address the valence correlations. In our calculations on the Pm I this is not very common as the $4f^{14}5s$ will not have two valence electrons if the f^{14} is to be closed. By allowing one excitation from the closed core the core-valence correlations will be addressed. Usually the outermost closed orbital will be excited as its energeticly favourable. This allows for CSFs such as $4f^{13}5s^2$ and $4f^{13}5s5p$ By allowing two electrons to excite from the core, core-core correlations can be addressed. This is however not implemented in the ASFs of these calculations as the CSF expansion would exceedingly big and the computing power needed is not available. As well good convergence becomes harder to achieve.

2.4 Spectroscopic orbitals

To improve calculations the GRASP has an option to choose which orbitals are spectroscopic and which are for correlation. The extra requirement on the spectroscopic orbital is that the number of nodes for the wave function is correct according to $n-l-1$. This is only true for orbitals occupying electrons. Correlation orbitals could have any number of nodes. It is not always possible to get convergence using this as it forces the right number of nodes throughout the whole calculation. A manual control at the end gives the same result.

3   Energy levels in the ion sequence

3.1   Setup and Procedure

To determine where in the Pm I sequence the spectra will become simple we want to look for when the simple states such as $4f^{14}5s$ become the lowest lying energy level. In theory the energy levels will have a linear dependence on Z so by varying this while looking at the energy for certain ASFs we can find where the spectra will become simple.

Starting with determining what energy levels can be interesting to study. In ground state Pm I has 61 electrons with the setup $4d^{10}5s^25p^66s^24f^5$. This state would be impossible to calculate with MCDF with so many valence electrons and open orbitals. As Z increases the electrons will be more tightly bound causing them to choose orbitals closer to the core. Minimizing N becomes more important than minimizing N+L. For example, the $4f^56s^2$ in Pm I will be $4f^66s$ in SM II where Z increased by 1 and so on. As we can't study these states it is better to start on the other end with the simplest and move up towards the ground state. 6 states will be studied in these calculations.

$4f^{14}5s$
$4f^{14}5p$
$4f^{13}5s^2$
$4f^{13}5s5p$
$4f^{12}5s^25p$
$4f^{11}5s^25p^2$

These states are the most likely to be among the lowest lying when getting close to the most simple states. Two different parts of the calculations were made. The first one is a simple Dirac Fock calculations with only the CSFs forming the specific state giving no correlation effects. Next step is then to include correlation orbitals using the MCDF-approach. As these calculations take more time and computer power initial DF-calculations were made to give a first overview of the system before more power was concentrated at the correct values of Z.

Next step is to decide what correlation orbitals are to be included in the multi configurational calculations. For each orbital included the CSF expansion grows and not all orbitals are usefull to the calculations. When doing calculations on serveral states balance in correlation must also be considered. Selecting the right orbitals is therefore critical for good results. Our states include 5s and 5p valance electrons. Correlation can only occur between states with equal parity. It's therefore only possible with jumps of $l = 2n$ for single excitations as $\pi = (-1)^{\sum l}$. This is not a problem for double excitation. The most likely correlation for 5s and 5p is therefore 5d and 5f. 5g is therefore excluded. Orbitals with $n = 6$ are the next to consider. The 6s and 6p orbitals will influence a lot. Including these in the $4f^{14}5s$ is no problem but doing this with $4f^{12}5s^25p$ for example would give a CSF expansion with around 250 000 CSFs. To get a proper balance the $n = 6$ orbitals were excluded.

Another factor discussed earlier is the number of allowed excitations from each orbital. All orbitals from 4d and below were closed for these calculations as an excitation from these orbitals would give us much higher energy. From 4f single excitations were allowed and from all $n = 5$ orbitals 2 excitations were allowed with a maximum of 2 total to limit the calculations while making sure most of the important correlations can be included.

During the calculations one has to choose what states to optimize on, denoted ASF serial in GRASP. For the lowest 1 is chosen, for the second lowest 2 and so on. All CSFs in the expansion will contribute to create the state with the given energy level in the order. If a lower lying state is included in the expansion one must take this into account. For example in $4f^{13}5s^2$ the $4f^{12}5s^25p$ CSFs are included as a single excitation from 4f to 5s is needed and the parity is the same. They have the J-values 5/2 and 7/2 in common. $4f^{12}5s^25p$ has 12 levels for 5/2 and 12 levels for 7/2 so if it's lower for a given Z, $4f^{13}5s^2$ will be level 13.
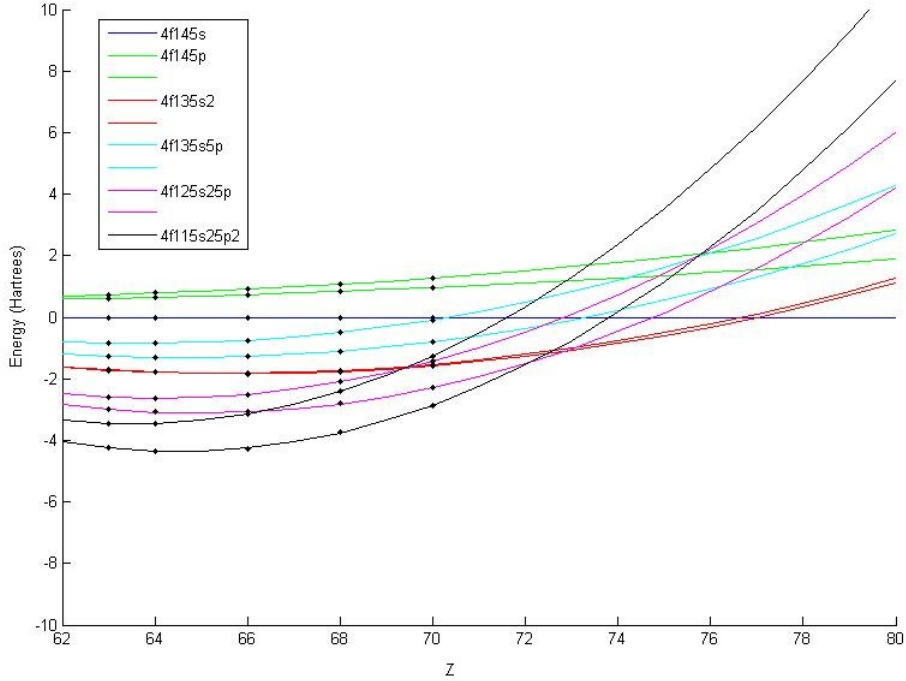
3.2 Results and discussion

Figure 1: Energy levels for the ion sequence

The first calculations made started at Z=63. Increasing with a few Z at a time to get several data points for each energy level to be able to create a regression for higher Z. This can be seen in figure 1. (Data from all calculations can be found in appendix). All states have 2 lines, the highest and the lowest level except for the $4f^{14}5s$ as it only has one level. $4f^{14}5s$ is in all figures set to zero energy as this is what is of interest. Another state that could be of interest is the $4f^{13}5s^2$ as it's relatively simple.

The area of interest is from Z=72 up to Z=78 for these two cases if the extrapolation is correct and correlation effects don't change way to much. The general outline of the energy levels look correct of what could be expected. $4f^{14}5s$ lower than $4f^{14}5p$ and $4f^{13}5s^2$ lower than $4f^{13}5s5p$ and the difference between them is quite close. An excitation from 5s to 5p should "cost" equally much.
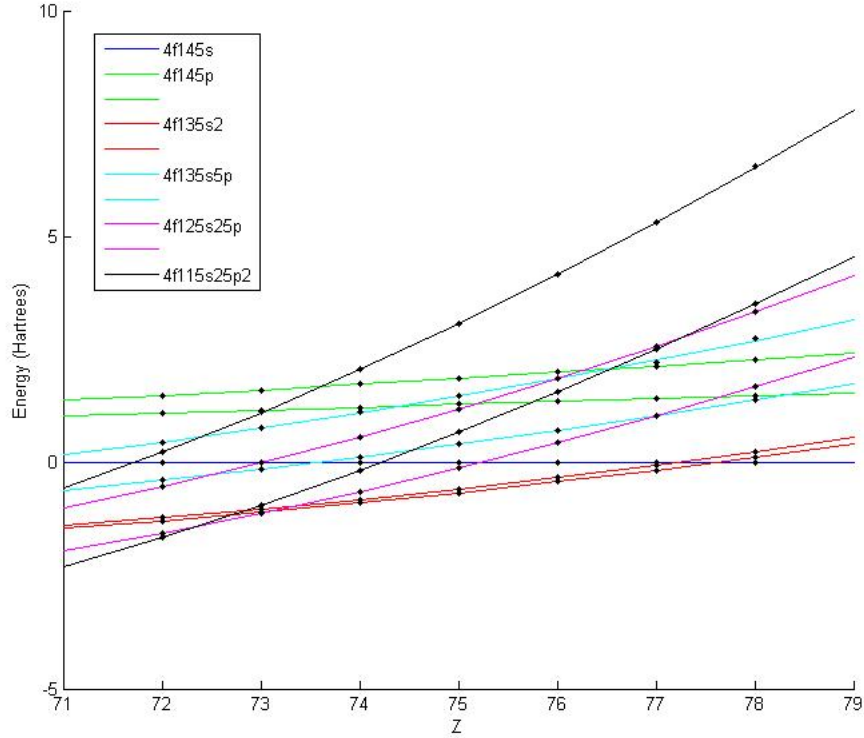
Figure 2: DF calculations

In the process of doing the MCDF calculations one has to do the single state DF-calculation to have the wave functions for the non correlation orbitals. Trying to optimize them all at one time will make convergence impossible. The correlation orbitals will therefore be added after the DF calculation. In figure 2 the DF results for Z=72 to Z=78 are shown.

In figure 3 the MCDF calculations are shown. QED effects are also included at this stage. As seen only a few states are included in this calculation. The $4f^{11}5s^25p^2$ and $4f^{12}5s^25p$ are really hard to get convergence on and are massive calculations. The general layout is the same so correlation did not have any major impacts. For the $4f^{13}5s5p$ at Z=72,73 one can see that the highest energy is much lower than before which seems very strange. When looking closer it was discovered that it had converged to the $4f^{12}5p5d5f$ state instead.

Doing the calculations for $4f^{13}5s^2$ it turned out not to be the lowest lying energy level for Z=72 but it was for Z=73. If ASF serial was set to 1 the $4f^{12}5s^25p$ state was found instead. This does not tell us that $4f^{12}5s^25p$ is lower for sure. The correlation for this state is not included in the CSF expansion for the calculation, since 4f11 is not possible from 4f13 as only one excitation from 4f was allowed. But this gives us a good hint where $4f^{13}5s^2$ becomes the lowest. An extra calculation on this was therefore attempted to try and find out if this was the case or if some more limitations are need.

	Z=73	Z=74
$4f^{13}5s^2$	-15544.206	-16073.316
$4f^{12}5s^25p$	-15544.374	-16073.008

With the help of a more powerful computer to do the calculation with over 80 000 CSFs in the expansion it was possible to get good convergence without any extra limitations.
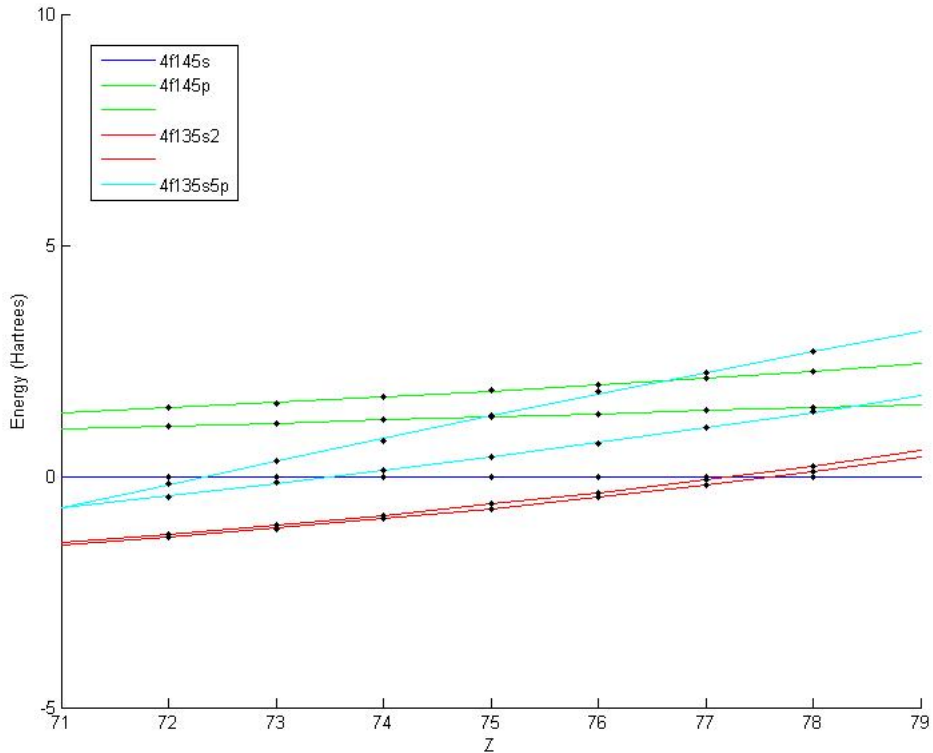
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Figure 3: MCDF calculations

The other area of interest is where $4f^{14}5s$ becomes the lowest. According to the data in figure 3 it's at Z=78 but not far from 77. Since both states involved are fairly simple an extra calculation was made to include $n = 6$ orbitals to see if more correlation would affect the results. Results showed that the effects were not big enough. The energy changed only by 0.01-0.02 hartrees when adding $n = 6$ while the splitting was in the order of 0.2 hartrees. These states are not very correlated.

Looking at the c^2 weights for $4f^{13}5s^2$ state the biggest correlation was the $4f^{13}5p^2$ CSF with in the order of 0.5% . It is possible that other states such as $4f^{12}5s^25p$ have more correlation and will therefore be affected more when adding $n = 6$. By looking at the difference from the DF to the MCDF with $n = 5$ for the two cases the change in $4f^{13}5s^2$ was about 0.02 hartree while the change for $4f^{12}5s^25p$ was 0.2 hartrees. Since the required energy needed to change the lowest energy level at Z=74 is around 0.3 hartrees more correlation could affect the results in a significant way.
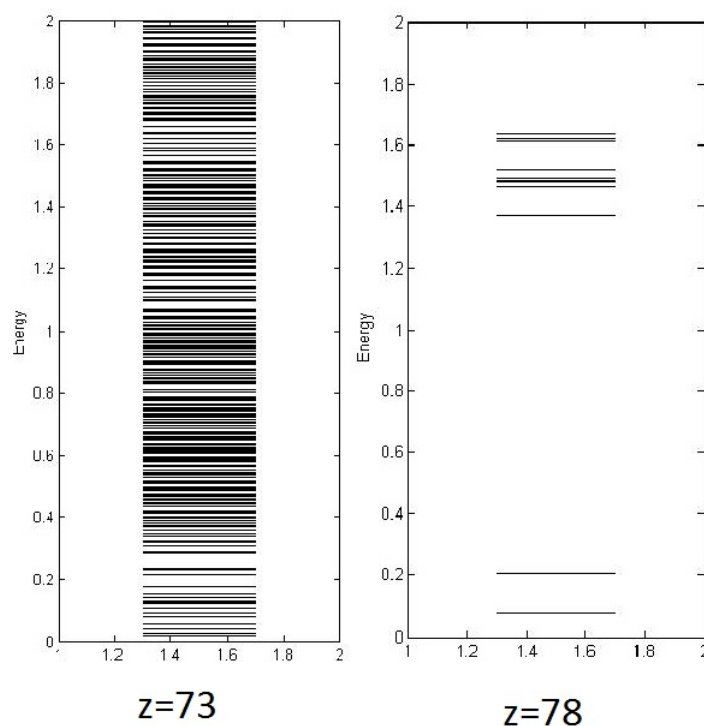
Figure 4: Energy level diagram(hartrees)

To give a better idea how the spectra would look at different Z simplified energy level diagrams were made for Z=73 and Z=78. Here it's very visible that the spectra for Z=73 still will be very complex. Even though a state with few levels is the lowest it will still have many possible transitions. Within 2 hartrees there are over 700 levels. There won't be transitions between all of these since most of them are forbidden but it will still be a forest of lines in the resulting spectra.

Looking at the Z=78 instead we see very few levels and only a few lines would make up the spectrum which would be easy to identify. As seen the lowest lying state is not a very important property for when the spectra becomes simple. There needs to be a gap up to the complex states as well to get few possible transitions as well.

4   Appendix

Z	$4f^{14}5s$	$4f^{14}5p$ h	$4f^{14}5p$ l	$4f^{13}5s^2$ h	$4f^{13}5s^2$ l
63	-10837,972	+0,738	+0,621	-1,712	-1,725
64	-11265,143	+0,783	+0,652	-1,769	-1,785
66	-12149,883	+0,911	+0,739	-1,812	-1,836
68	-13075,368	+1,080	+0,848	-1,730	-1,765
70	-14041,987	+1,275	+0,968	-1,528	-1,576
72	-15050,298	+1,496	+1,095	-1,216	-1,280
73	-15570,284	+1,613	+1,159	-1,024	-1,098
74	-16100,946	+1,737	+1,225	-0,810	-0,893
75	-16642,380	+1,866	+1,291	-0,574	-0,668
76	-17194,674	+2,002	+1,358	-0,317	-0,422
77	-17757,982	+2,143	+1,425	-0,042	-0,159
78	-18332,381	+2,291	+1,494	+0,253	+0,123

Z	$4f^{13}5s5p$ h	$4f^{13}5s5p$ l	$4f^{12}5s^25p$ h	$4f^{12}5s^25p$ l	$4f^{11}5s^25p^2$ h	$4f^{11}5s^25p^2$ l
63	-0,845	-1,266	-2,593	-2,996	-3,444	-4,246
64	-0,851	-1,297	-2,628	-3,085	-3,458	-4,353
66	-0,750	-1,266	-2,508	-3,084	-3,160	-4,261
68	-0,488	-1,094	-2,103	-2,810	-2,410	-3,744
70	-0,080	-0,794	-1,435	-2,290	-1,261	-2,856
72	+0,459	-0,384	-0,535	-1,556	+0,242	-1,649
73	+0,772	-0,143	-0,007	-1,118	+1,113	-0,940
74	+1,113	+0,121	+0,572	-0,636	+2,061	-0,166
75	+1,481	+0,407	+1,197	-0,112	+3,080	+0,671
76	+1,876	+0,713	+1,869	+0,451	+4,170	+1,566
77	+2,209	+1,036	+2,583	+1,051	+5,327	+2,516
78	+2,740	+1,380	+3,341	+1,687	+6,551	+3,519

Tables with energies from Dirac Fock calculations. (Hartrees)
$4f^{14}5s$ gives full value, rest is difference relative.

Z	$4f^{14}5s$	$4f^{14}5p$ h	$4f^{14}5p$ l	$4f^{13}5s^2$ h	$4f^{13}5s^2$ l	$4f^{13}5s5p$ h	$4f^{13}5s5p$ l
72	-15024,387	+1,482	+1,080	-1,248	-1,311	-0,170	-0,445
73	-15543,077	+1,586	+1,149	-1,059	-1,129	+0,345	-0,142
74	-16072,396	+1,722	+1,219	-0,841	-0,920	+0,777	+0,127
75	-16612,434	+1,850	+1,283	-0,605	-0,695	+1,319	+0,413
76	-17163,282	+1,987	+1,351	-0,347	-0,447	+1,826	+0,721
77	-17725,093	+2,128	+1,419	-0,067	-0,179	+2,249	+1,048
78	-18297,939	+2,276	+1,487	+0,228	+0,103	+2,696	+1,393

Tables with energies from MCDF calculations. (Hartrees)
$4f^{14}5s$ gives full value, rest is difference relative.

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