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**The effect of self-consistent potentials on EXAFS analysis**

**B. Ravel, M. Newville, J. J. Kas and J. J. Rehr**

# The effect of self-consistent potentials on EXAFS analysis

## Supplemental Materials

Bruce Ravel, Matt Newville

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# 1 Background

(Please note that underlined, blue text indicates a web link in this PDF document.)

In a [recent post](#) to the [IFEFFIT mailing list](#), a poor soul made this comment:

I wondering about the availability to use a newer FEFF version in Demeter. Since my knowledge only I can run FEFF6. In my case I found different discrepancies using FEFF6 and FEFF9 in the determination of bond length distances for instance. In terms of review of papers, reviewers ask to use a newer version instead FEFF6.

This is a topic that comes up regularly on the mailing list. We decided to investigate the effect of different theory models on EXAFS analysis.

Because FEFF9 is not freely available and redistributable, it is hard to make use of it in the manner of this exercise. Consequently, the forms of FEFF used here are the two redistributable versions: the FEFF6 that comes with [IFEFFIT](#) and [FEFF85L](#).

These results were presented at a [recent symposium on theoretical spectroscopy](#). By far, the most illuminating comment was from Alexei Ankudinov, the principle author of FEFF8. Alex was surprised that anyone expected FEFF8 or FEFF9 to make a difference for EXAFS analysis. Most of the features in those later versions, and particularly in FEFF9, pertain to calculations of other spectroscopies. Other new additions to the code would not be expected to have much impact for photoelectrons of high kinetic energy, i.e. far from the absorption edge.

This document is about *EXAFS* analysis, not XANES calculations or calculations of other spectroscopies. Obviously, any calculation of a spectroscopy for which the photoelectron has low kinetic energy will be extremely sensitive to the details of the potential surface. Self-consistency and charge transfer are [unambiguously important](#) for such calculations. The question here is about the impact on the analysis of the EXAFS spectrum.

Be all that as it may, the “FEFF8/FEFF9 **must** be better” comment is perennial. This is an attempt to address that question with some kind of rigorous effort.

Here are the conditions of the tests:

1. All XAS data were processed sensibly in [ATHENA](#) with  $E_0$  chosen to be the first peak of the first derivative in  $\mu(E)$ . That may not be the best choice of  $E_0$  in all cases, but it is the obvious first choice and the likeliest choice to be made by a novice user of the software.
2. All EXAFS data were Fourier transformed starting at  $3 \text{ \AA}^{-1}$  and ending at a reasonable place where the signal was still much bigger than the noise. The choice of  $3 \text{ \AA}^{-1}$  as the starting point was deliberate. The [AUTOBK algorithm](#) (and, indeed, all other background removal algorithms) is often unreliable below about  $3 \text{ \AA}^{-1}$  due to the fact that the  $\mu(E)$  is changing very quickly in that region. Thus the data above  $3 \text{ \AA}^{-1}$  are likely to be reliably free of systematic error due to the details of the background removal.
3. All the materials considered have well-known structures. For these tests, we want to avoid the situation where error in a fitting model could be attributed to incomplete prior knowledge about the structure. That is, we want to isolate the details of the fitting model from the details of the theoretical calculation.

4. The first three examples are dense, crystalline solids for which one expects self-consistency to contribute rather little to the analysis. The remaining materials all contribute interesting features for which self-consistency and charge transfer might play a role.
5. In the plots, the ranges of the Fourier transform and of the fit are indicated by vertical black lines.
6. Each material is fitted using theory from the version of FEFF6 that ships with `IFEFFIT`, from `FEFF85L` with self-consistency turned off, and from with `FEFF85L` with self-consistency. In each case, the default self-energy model (Hedin-Lundqvist) was used.
7. For each material that is not a molecule, the analysis is done with a sequence of self-consistency radii. This is done to test the importance of the consideration of that parameter on the analysis. In the case of hydrated uranyl hydrate, this is a molecule, but the FEFF calculation is made on a crystalline analogue to the molecule. The effect of self-consistency radius is tested in that case.
8. For molecules (bromoadamantane, for example), the `lfms` parameter of the SCF card is set to 1.
9. The uranyl calculation was a bit challenging with `FEFF85L`. To get the program to run to completion, it was necessary to set the `FOLP` parameter to 0.9 for each unique potential. Given that the quality of the fit was much the same as for using FEFF6, this was not examined further. Still, this merits further attention for this material.
10. All fits were performed with a toolset written by Bruce and using the XAS analysis capabilities of `LARCH`.
11. All uncertainties are  $1\sigma$  error bars determined from the diagonal elements of the covariance matrix evaluated during the Levenberg-Marquardt minimizations.
12. The plots shown below for each material were generated automatically after each fit. You will notice that they appear to be highly repetitive. For each material it is the case that the fits using the different theoretical models are nearly indistinguishable by eye. The full complement of fits are shown. Looking through the plots of the fit results, you may be tempted to think that the same image has been replicated several times. We assure you that each plot is actual plot made using the actual fit to the different theory models!
13. The very astute FEFF user might point out that the path indexing is not guaranteed to be consistent across versions. That is, a small MS path may barely exceed the heap criterion in one version of FEFF, but not in another. That would change the indexing for all paths with longer half-path-lengths, thus confounding the use of single `LARCH` fitting script with the different version of the theory. To avoid this problem, the pathfinder in FEFF6 was run, generating a `paths.dat` file. This `paths.dat` was then copied into the folders where the various `FEFF85L` calculations were run. The pathfinder was then skipped in each of the FEFF8 runs. This guaranteed that each theory calculation generated the same list of `feffNNNN.dat` files with the same indexing.

14. For each material, a table of charge transfer and threshold energies is presented. This is information gleaned from FEFF8's screen messages and FEFF6's standard header. The charge transfer values are the final charge transferred for each unique potential as reported in the final round of the self-consistency loop. The threshold energy  $\mu$  is reported for each self-consistency radius as well as for FEFF8 without self-consistency and for FEFF6. This table is provided in hopes that it might help make sense of the fitted values for  $E_0$ . Any connections seem unclear, however.

## 2 Copper

The data is the copper foil spectrum attributed to [Matt Newville's PhD thesis](#). The fitting model is very simple. There is an  $S_0^2$  parameter (**amp**), an energy shift for all paths (**enot**), and a volumetric lattice expansion coefficient (**alpha**). The  $\sigma^2$  values for all paths were computed using the correlated Debye model and a temperature of 10K, except for the first shell, which has its own  $\sigma^2$  variable (**ss1**).

The fit included 4 coordination shells, which includes several co-linear multiple scattering paths of the same distance as the fourth shell single scattering path.

**amp** and **alpha** are unitless. **enot** is eV, **ss1** is  $\text{\AA}^2$ , and **thetad** is K.

### 2.1 Best fit values

model	alpha	amp	enot	ss1	thetad
feff6	-0.00074(92)	0.96(4)	4.97(49)	0.00382(33)	253(22)
noSCF	-0.00046(90)	0.95(4)	5.71(48)	0.00400(33)	239(19)
withSCF(3)	-0.00077(104)	0.94(5)	3.45(56)	0.00402(38)	241(22)
withSCF(4)	-0.00076(104)	0.94(5)	3.54(56)	0.00402(38)	242(22)
withSCF(5)	-0.00077(104)	0.94(5)	3.40(56)	0.00402(38)	241(22)
withSCF(5.5)	-0.00077(105)	0.94(5)	3.41(56)	0.00402(38)	241(22)
withSCF(6)	-0.00076(104)	0.94(5)	3.46(56)	0.00402(38)	241(22)

### 2.2 Statistics

model	$\chi^2$	reduced $\chi^2$	R-factor
feff6	1444.2957	54.3832	0.0145
noSCF	1414.0154	53.2430	0.0142
withSCF(3)	1820.7826	68.5594	0.0182
withSCF(4)	1814.3186	68.3160	0.0182
withSCF(5)	1816.7825	68.4088	0.0182
withSCF(5.5)	1823.5990	68.6654	0.0183
withSCF(6)	1819.3955	68.5071	0.0182

### 2.3 Charge transfer and threshold energy

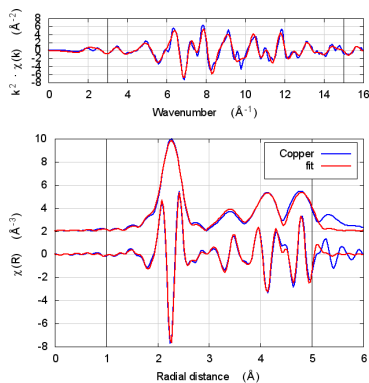
ip	R=3	R=4	R=5	R=5.5	R=6
0	-0.527	-0.524	-0.512	-0.523	-0.516
1	0.005	0.005	0.005	0.005	0.005
$\mu$	-8.091	-7.964	-8.104	-8.124	-8.056

Starting value for  $\mu$  in FEFF8 = -3.820

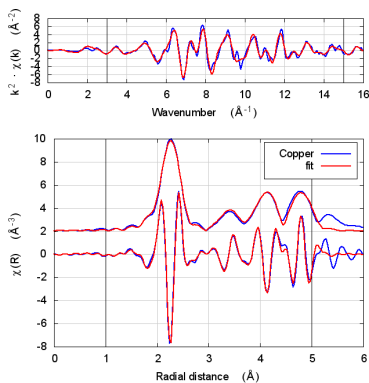
Value for  $\mu$  in FEFF6 = -5.519

## 2.4 Fits

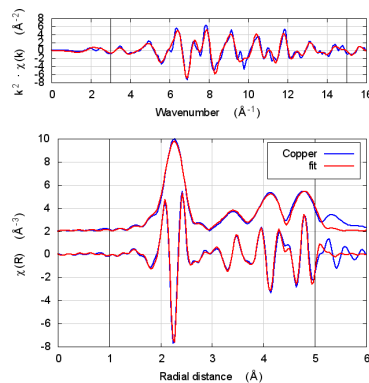
feff6



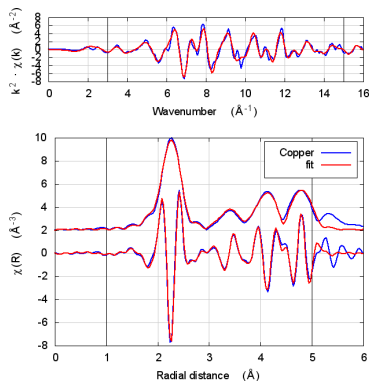
no SCF



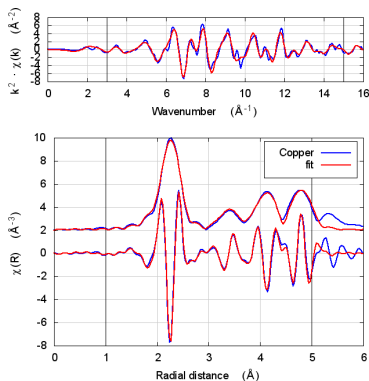
SCF, R=3



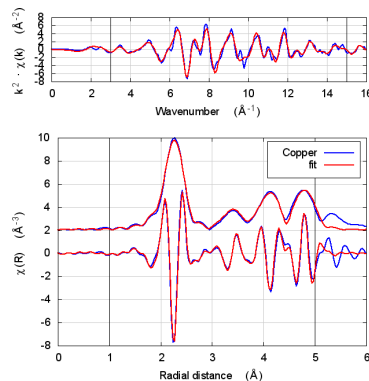
SCF, R=4



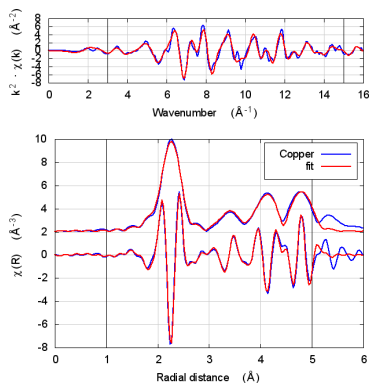
SCF, R=5



SCF, R=5.5



SCF, R=6



## 2.5 Discussion

We start with copper because all discussions of XAS theory start with copper. It's tradition!

In fact, one expects copper to be a null result. There is no reason to expect that charge transfer and self-consistency would have much effect on a monoatomic material. That expectation is borne out.

The fitting parameters are constant well within their uncertainties and across all theory models.



The statistical parameters also do not change much across the models. Amusingly, reduced  $\chi^2$  and R-factor are a bit smaller *without* the use of self-consistency.

### 3 NiO

The sample was NiO powder prepared by Neil Hyatt (University of Sheffield) and checked by him for phase purity. The powder was mixed with polyethylene glycol and pressed into a pellet to make a edge step of 0.78. The data were measured by Bruce at NSLS beamline X23A2 and reported in a recent issue of Journal of Synchrotron Radiation: DOI: [10.1107/S1600577515013521](https://doi.org/10.1107/S1600577515013521). The simple fitting model to this rock salt structure included a  $S_0^2$  parameter (**amp**), an energy shift (**enot**), and a volumetric lattice expansion coefficient (**alpha**).

The fit included 4 coordination shells, 2 with O and 2 with Ni. There are several co-linear multiple scattering paths at the same distance as the fourth shell Ni scatterer. Each shell has its own  $\sigma^2$  parameter (**sso**, **ssni**, **sso2**, and **ssni2**, respectively).

**amp** and **alpha** are unitless. **enot** is eV. **sso**, **ssni**, **sso2**, and **ssni2** are  $\text{\AA}^2$ .

#### 3.1 Best fit values

model	alpha	amp	enot	ssni	ssni2	sso	sso2
feff6	0.00062(146)	0.71(5)	-1.22(54)	0.00546(56)	0.00714(95)	0.00437(120)	0.04205(3218)
noSCF	0.00050(152)	0.68(5)	2.49(56)	0.00534(58)	0.00715(101)	0.00468(131)	0.03946(2918)
withSCF(2.5)	-0.00021(148)	0.71(4)	-7.34(54)	0.00554(56)	0.00726(97)	0.00468(123)	0.03146(2038)
withSCF(3)	-0.00073(145)	0.71(4)	-7.95(53)	0.00555(55)	0.00715(95)	0.00456(119)	0.03368(2237)
withSCF(3.7)	-0.00068(145)	0.71(4)	-7.94(53)	0.00555(55)	0.00716(95)	0.00457(119)	0.03344(2213)
withSCF(4.2)	-0.00010(149)	0.71(4)	-7.29(55)	0.00554(56)	0.00727(98)	0.00470(124)	0.03099(1996)
withSCF(4.7)	-0.00023(148)	0.71(4)	-7.31(54)	0.00554(56)	0.00725(97)	0.00466(123)	0.03167(2060)

#### 3.2 Statistics

model	$\chi^2$	reduced $\chi^2$	R-factor
feff6	27430.3658	1347.4609	0.0215
noSCF	29860.6446	1466.8434	0.0234
withSCF(2.5)	28069.2786	1378.8462	0.0220
withSCF(3)	26875.8980	1320.2238	0.0211
withSCF(3.7)	26950.4623	1323.8866	0.0211
withSCF(4.2)	28301.4677	1390.2520	0.0222
withSCF(4.7)	28050.1096	1377.9046	0.0220

#### 3.3 Charge transfer and threshold energy

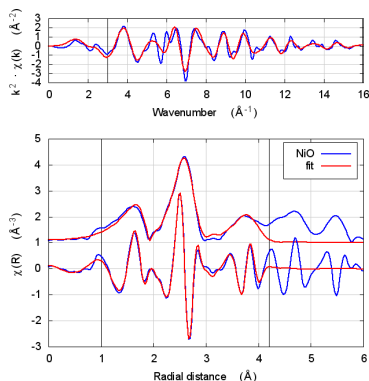
ip	R=2.5	R=3	R=3.7	R=4.2	R=4.7
0	0.084	0.150	0.145	0.092	0.080
1	0.090	0.177	0.171	0.092	0.104
2	-0.091	-0.179	-0.172	-0.093	-0.105
$\mu$	-12.012	-12.768	-12.749	-11.952	-11.973

Starting value for  $\mu$  in FEFF8 = -3.100

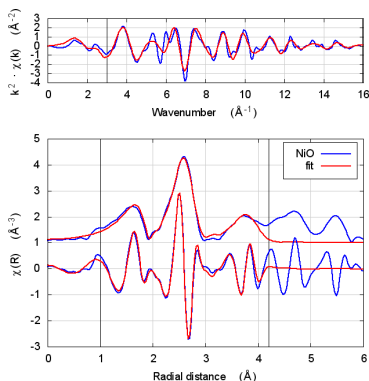
Value for  $\mu$  in FEFF6 = -3.478

### 3.4 Fits

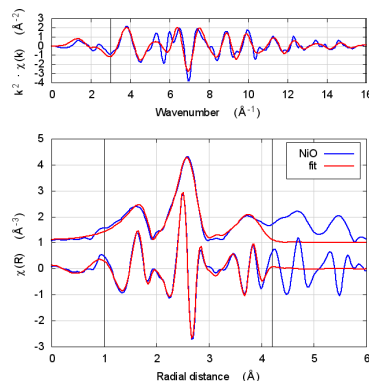
feff6



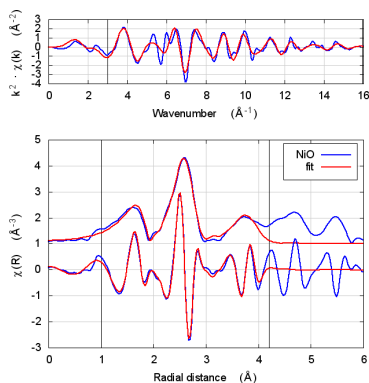
no SCF



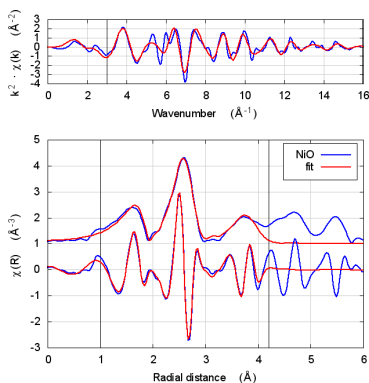
SCF, R=2.5



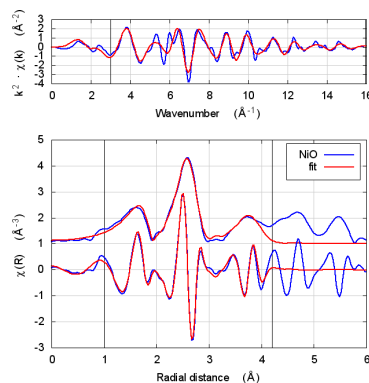
SCF, R=3



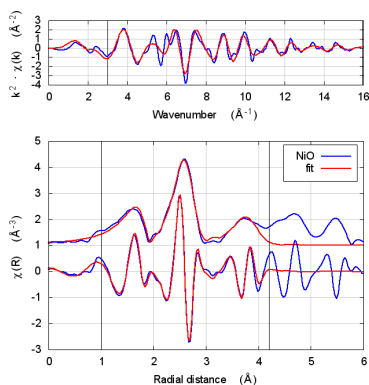
SCF, R=3.7



SCF, R=4.2



SCF, R=4.7



### 3.5 Discussion

NiO was chosen as the second example because it constitutes the smallest added complexity compared to copper. NiO is a rock salt structure, so it is highly ordered and the local configuration around the Ni atom is very well known. With an oxygen ligand, there should be some charge transfer.

With the exception of the  $E_0$  parameter, all of the parameters are constant well within their

error bars. The statistical parameters are unchanged from model to model.

This is the first example of dependence of the  $E_0$  parameter on theoretical model. The ultimate value of FEFF's threshold energy depends on the model. The starting condition is not the same in FEFF6 as in FEFF8 without self-consistency. This is seen by the 3.3 eV shift in fitted  $E_0$  value. Furthermore, the threshold changes as charge is transferred and self-consistency is reached. This results in a -6 eV shift relative to FEFF6.

An explanation of the  $E_0$  fitting parameter is that it is the parameter that lines up the zero of wavenumber in the data with the zero of wavenumber in the theory. As such, it is hard to say that one of these  $E_0$  results is "better" than the others.

One might hope that improvements in theory would lead to a fitted  $E_0$  parameter of 0 when the edge is chosen at the inflection point of the rising edge of the XAS data. While that might be true, we're not there yet with FEFF8. See the conclusion for more discussion.

## 4 FeS<sub>2</sub>

This is a [teaching example](#). It's good for teaching as it is fairly simple – it's cubic – but it has a bit of structure and two kinds of scatterers. The data are taken from [Matt Newville's online collection of reference data](#).

The model includes a  $S_0^2$  parameter (**amp**), an energy shift (**enot**), and a volumetric lattice expansion coefficient (**alpha**). The first and second shell S scatterers each get a  $\sigma^2$  parameter (**ss** and **ss2**). The third shell of S atoms only contains 2 scatterers. In practice, floating its  $\sigma^2$  parameter independently does not yield a statistical improvement to the fit, so the **ss2** parameter is used for the third shell  $\sigma^2$ . Finally a  $\sigma^2$  parameter is floated for the Fe shell.

The fitting model includes a variety of multiple scattering paths, including a triangle between the first shell S and the fourth shell Fe, and four paths that bounce around among first shell S atoms.

**amp** and **alpha** are unitless. **enot** is eV. **ss**, **ss2**, and **ssfe** are Å<sup>2</sup>.

### 4.1 Best fit values

model	alpha	amp	enot	ss	ss2	ssfe
feff6	0.00092(126)	0.69(2)	2.77(42)	0.00296(41)	0.00366(106)	0.00484(50)
noSCF	0.00183(171)	0.65(3)	7.01(57)	0.00294(57)	0.00386(151)	0.00471(68)
withSCF(3)	0.00219(191)	0.68(3)	-2.01(63)	0.00311(63)	0.00422(172)	0.00495(77)
withSCF(3.6)	0.00212(188)	0.68(3)	-2.15(62)	0.00311(62)	0.00423(170)	0.00495(76)
withSCF(4)	0.00212(191)	0.68(3)	-2.17(63)	0.00311(63)	0.00423(172)	0.00494(77)
withSCF(5.3)	0.00216(194)	0.68(4)	-1.92(64)	0.00310(64)	0.00421(175)	0.00493(78)
withSCF(5.5)	0.00216(194)	0.68(4)	-1.88(64)	0.00310(64)	0.00421(175)	0.00493(78)

### 4.2 Statistics

model	$\chi^2$	reduced $\chi^2$	R-factor
feff6	2052.3016	146.4407	0.0064
noSCF	3783.2180	269.9491	0.0119
withSCF(3)	4639.2799	331.0329	0.0146
withSCF(3.6)	4502.7226	321.2889	0.0141
withSCF(4)	4634.9046	330.7207	0.0145
withSCF(5.3)	4778.2793	340.9511	0.0150
withSCF(5.5)	4798.0987	342.3653	0.0151

### 4.3 Charge transfer and threshold energy

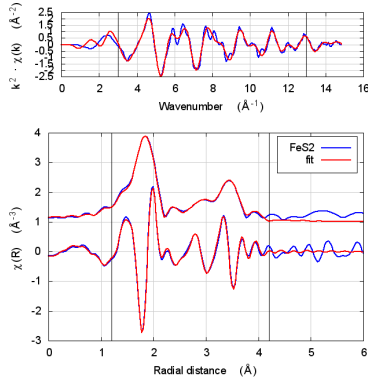
ip	R=3	R=3.6	R=4	R=5.3	R=5.5
0	-0.332	-0.346	-0.359	-0.378	-0.376
1	-0.325	-0.346	-0.380	-0.396	-0.397
2	0.164	0.175	0.192	0.200	0.201
$\mu$	-9.464	-9.555	-9.671	-9.488	-9.465

Starting value for  $\mu$  in FEFF8 = -0.796

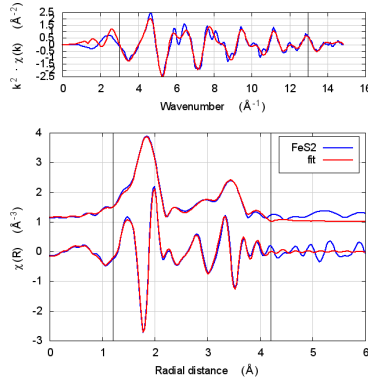
Value for  $\mu$  in FEFF6 = -4.308

## 4.4 Fits

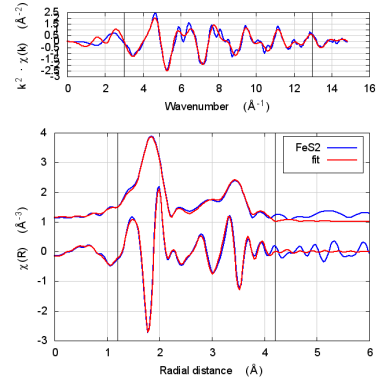
feff6



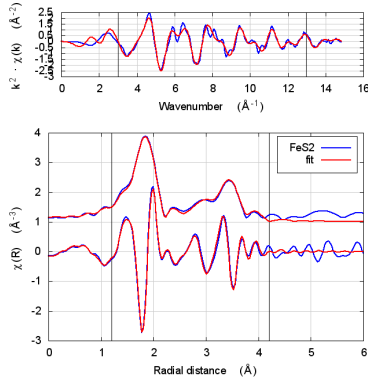
no SCF



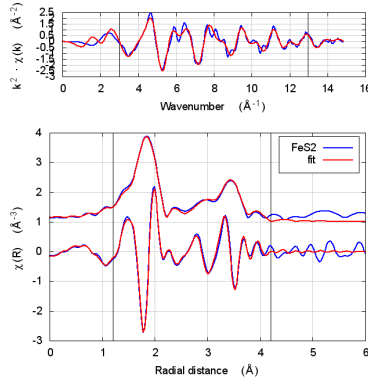
SCF, R=3



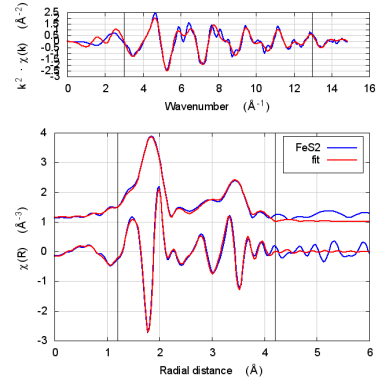
SCF, R=3.6



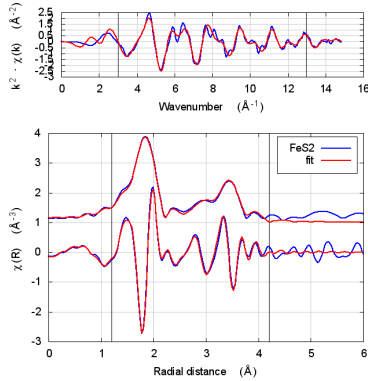
SCF, R=4



SCF, R=5.3



SCF, R=5.5



## 4.5 Discussion

This is just slightly more complex than NiO. It is diatomic, but with a slightly less orderly structure than NiO. Again, all parameters except for  $E_0$  are consistent within uncertainty, although the  $\alpha$  parameter does show some correlation with  $E_0$ . All other parameters are essentially unchanged.

The  $E_0$  parameter, with self-consistency, is equally far from 0 as for FEFF6, although with a sign change.

There are a small handful of small MS paths with half-path-lengths within the fitting range but which are not included in this fit. This may account for the increase in reduced  $\chi^2$  and R-factor between FEFF6 and FEFF8.

## 5 UO<sub>2</sub>

The data are the UO<sub>2</sub> shown in [DOI: 10.1021/es0208409](https://doi.org/10.1021/es0208409)

This is an interesting test as it is an *f*-electron system.

The fitting model follows rather closely to what is described in that paper, particularly the content of Table 2, although  $S_0^2$  is allowed to float (`amp`). Along with an energy shift (`enot`), a  $\Delta R$  and  $\sigma^2$  for the first shell O (`dro` and `sso`), a  $\Delta R$  and  $\sigma^2$  for the second shell U (`dru` and `ssu`), and a  $\Delta R$  and  $\sigma^2$  for the third shell O (`dro2` and `sso2`), there is a parameter for the number of U scatterers (`nu`).

The model includes the same 6 paths given in Table 2 of the paper.

`amp` is unitless. `enot` is eV. `dro`, `dru`, and `dro2` are Å. `sso`, `ssu`, and `sso2` are Å<sup>2</sup>.

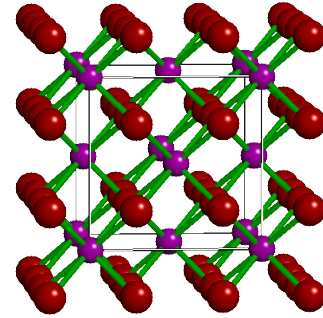


Figure 1: Uraninite

### 5.1 Best fit values

model	amp	dro	dro2	dru	enot	nu	sso	sso2	ssu
feff6	0.87(11)	-0.022(14)	-0.055(24)	0.005(11)	4.87(136)	11.43(481)	0.00939(213)	0.01060(440)	0.00488(247)
noSCF	0.84(11)	-0.023(15)	-0.024(32)	0.001(12)	8.15(146)	9.27(416)	0.00872(221)	0.01061(618)	0.00382(273)
withSCF(3)	0.84(10)	-0.026(13)	-0.013(28)	-0.002(11)	1.63(129)	9.21(376)	0.00894(209)	0.00976(511)	0.00393(250)
withSCF(4)	0.84(10)	-0.026(13)	-0.013(29)	-0.003(11)	2.08(130)	9.16(373)	0.00892(209)	0.00972(513)	0.00389(250)
withSCF(5)	0.84(10)	-0.026(13)	-0.012(28)	-0.003(11)	1.72(129)	9.18(373)	0.00893(208)	0.00969(508)	0.00391(249)
withSCF(5.5)	0.84(10)	-0.026(13)	-0.012(28)	-0.003(11)	1.62(129)	9.17(372)	0.00894(208)	0.00970(509)	0.00391(249)
withSCF(6)	0.84(10)	-0.026(13)	-0.012(29)	-0.003(11)	1.71(129)	9.16(372)	0.00893(208)	0.00971(510)	0.00390(249)

### 5.2 Statistics

model	$\chi^2$	reduced $\chi^2$	R-factor
feff6	166.2736	22.0712	0.0160
noSCF	188.4320	25.0125	0.0181
withSCF(3)	169.5918	22.5116	0.0163
withSCF(4)	169.9560	22.5600	0.0163
withSCF(5)	169.1192	22.4489	0.0163
withSCF(5.5)	169.1306	22.4504	0.0163
withSCF(6)	169.2412	22.4651	0.0163

### 5.3 Charge transfer and threshold energy

ip	R=3	R=4	R=5	R=5.5	R=6
0	1.122	1.146	1.180	1.189	1.191
1	0.715	0.726	0.740	0.745	0.741
2	-0.363	-0.369	-0.376	-0.379	-0.377
$\mu$	-8.541	-8.114	-8.522	-8.624	-8.542

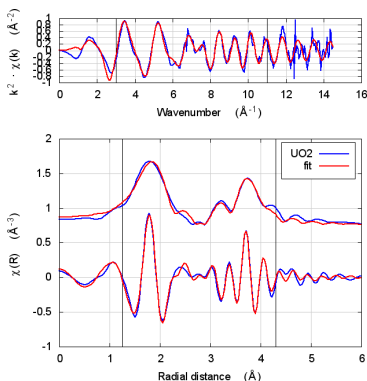
Starting value for  $\mu$  in FEFF8 = -0.640

Value for  $\mu$  in FEFF6 = -6.058

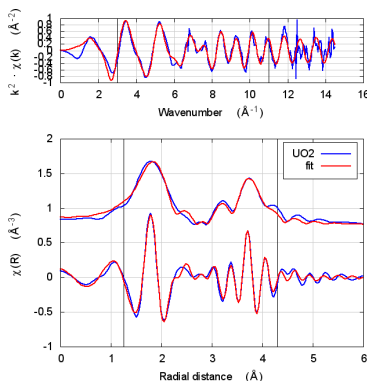


## 5.4 Fits

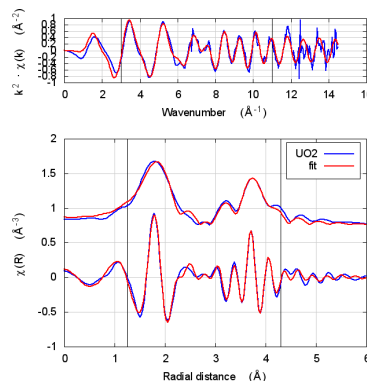
feff6



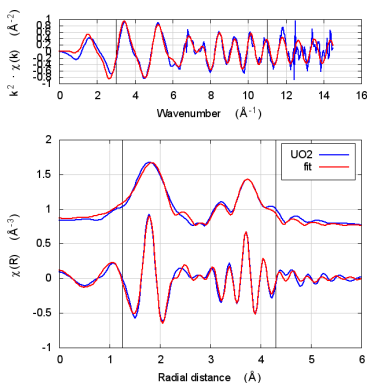
no SCF



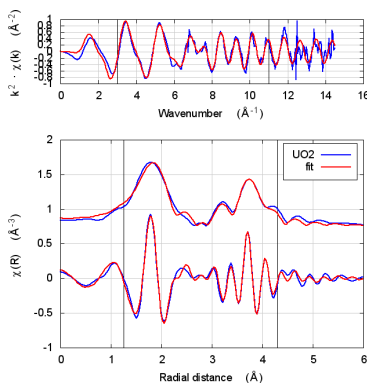
SCF, R=3



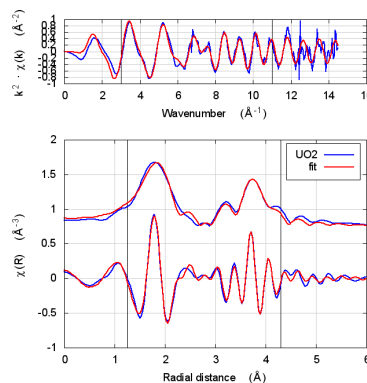
SCF, R=4



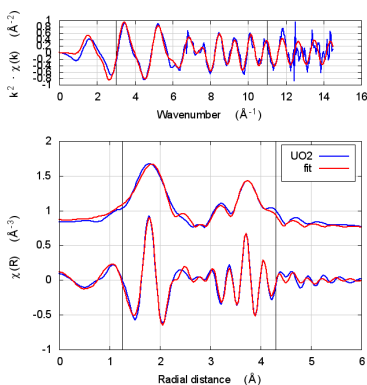
SCF, R=5



SCF, R=5.5



SCF, R=6



## 5.5 Discussion

The first thing to notice about  $\text{UO}_2$  is that the statistical parameters of the fit are completely unchanged between theory models.

This  $E_0$  parameter is the first one that behaves in the expected way – with self-consistency and charge transfer, the fitted  $E_0$  ends up closer to 0. Perhaps this is a hint that self-consistency is important for  $f$ -electron systems.

All of the other fitting parameters are unchanged within their uncertainties. One parameter merits a bit more discussion. In the paper cited above, the fitted value of  $\nu$ , i.e. the partial occupancy of the U atom in the second scattering shell, is used to say something about the size of the uraninite nanoparticles generated by the reduction process. While the fitted value of  $\nu$  does not change outside of its very large uncertainty, it does change substantively. This would likely effect the interpretation of the fitting results in the context of the reduction process.

## 6 BaZrO<sub>3</sub>

In a short paper on the Zr edge of BaZrO<sub>3</sub>, DOI: [10.1016/0921-4526\(94\)00654-E](https://doi.org/10.1016/0921-4526(94)00654-E), Haskel et al. proposed that shortcomings of FEFF's potential model could be accommodated by floating an energy shift parameter for each scatterer species. The concept is that doing so approximates the effect of errors in the scattering phase shifts.

The data are the same as in that paper, although the fitting model is slightly different. Rather than floating  $\Delta R$  parameters for each shell, a volumetric expansion coefficient (**alpha**) is used. Along with  $S_0^2$  (**amp**), there are energy shifts for each scatterer (**enot**, **eZR**, and **eba**) and  $\sigma^2$  parameters for each scatterer (**sso**, **sszr**, and **ssba**). The fourth shell O is included in the fit. It gets a  $\sigma^2$  (**sso2**) but uses the energy shift for the O scatterer.

BaZrO<sub>3</sub> is a true perovskite. Zr sites in the octahedral B site. A variety of co-linear multiple scattering paths at the distance of the third shell Zr scatterer are included in the fit. The energy shifts are parameterized as described in the paper.

**amp** and **alpha** are unitless. **enot**, **eZR**, and **eba** are eV. **sso**, **sszr**, **ssba**, and **sso2** are Å<sup>2</sup>.

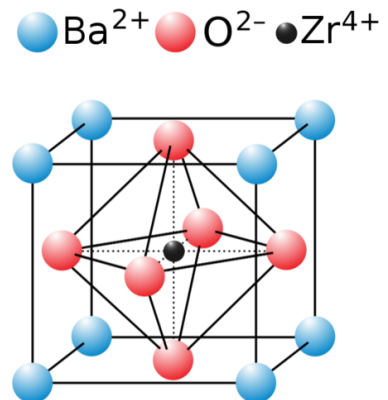


Figure 2: The perovskite structure.

### 6.1 Best fit values

model	alpha	amp	eba	enot	eZR	ssba	sso	sso2	sszr
feff6	-0.00032(85)	1.22(7)	-9.906(567)	-8.55(57)	-5.597(1717)	0.00561(37)	0.00403(70)	0.00908(253)	0.00413(33)
noSCF	0.00044(86)	1.07(6)	-3.901(589)	-2.32(58)	0.946(1886)	0.00530(38)	0.00361(70)	0.00791(242)	0.00369(34)
withSCF(3)	-0.00007(72)	1.13(5)	-10.768(469)	-10.52(47)	-6.682(1580)	0.00561(32)	0.00382(58)	0.00855(208)	0.00362(28)
withSCF(4)	-0.00007(74)	1.13(5)	-11.026(482)	-10.60(48)	-6.794(1618)	0.00559(33)	0.00380(59)	0.00850(213)	0.00362(28)
withSCF(5)	-0.00007(73)	1.13(5)	-11.094(479)	-10.81(48)	-7.057(1604)	0.00561(33)	0.00381(59)	0.00850(211)	0.00363(28)
withSCF(5.5)	-0.00007(73)	1.13(5)	-10.950(477)	-10.77(48)	-7.050(1594)	0.00562(33)	0.00382(59)	0.00850(210)	0.00364(28)
withSCF(6)	-0.00005(73)	1.13(5)	-10.705(474)	-10.49(48)	-6.726(1590)	0.00562(33)	0.00382(59)	0.00851(208)	0.00364(28)

### 6.2 Statistics

model	$\chi^2$	reduced $\chi^2$	R-factor
feff6	8979.2479	555.6561	0.0108
noSCF	9536.0604	590.1130	0.0114
withSCF(3)	6579.0004	407.1234	0.0079
withSCF(4)	6898.9084	426.9200	0.0083
withSCF(5)	6837.1517	423.0984	0.0082
withSCF(5.5)	6790.5892	420.2170	0.0081
withSCF(6)	6690.0972	413.9983	0.0080

### 6.3 Charge transfer and threshold energy

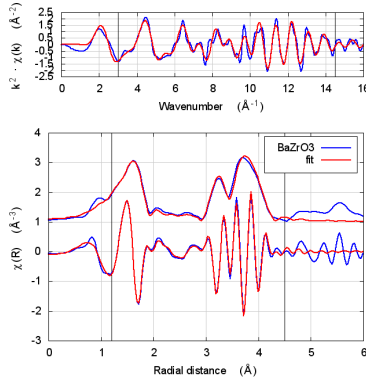
ip	R=3	R=4	R=5	R=5.5	R=6
0	0.250	0.313	0.279	0.244	0.218
1	0.607	0.546	0.607	0.653	0.628
2	0.535	0.561	0.528	0.495	0.494
3	-0.381	-0.370	-0.379	-0.383	-0.375
$\mu$	-7.698	-7.958	-8.036	-7.902	-7.600

Starting value for  $\mu$  in FEFF8 = -1.336

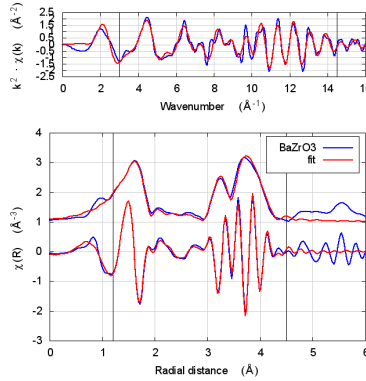
Value for  $\mu$  in FEFF6 = -6.654

## 6.4 Fits

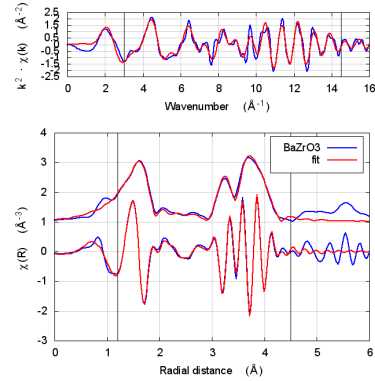
feff6



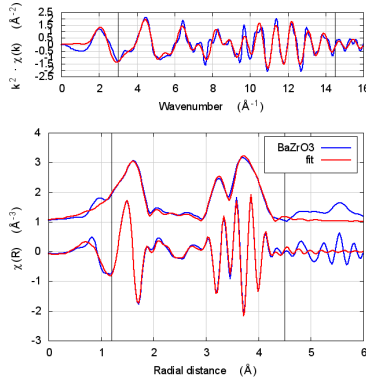
no SCF



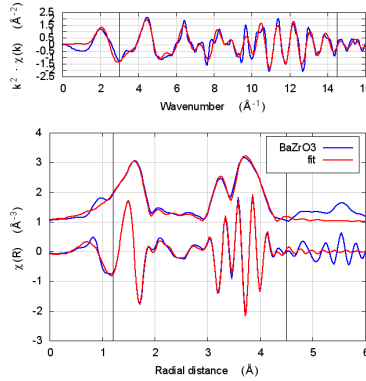
SCF, R=3



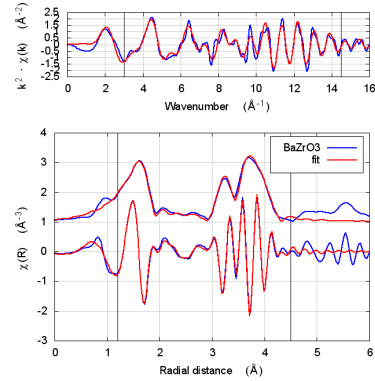
SCF, R=4



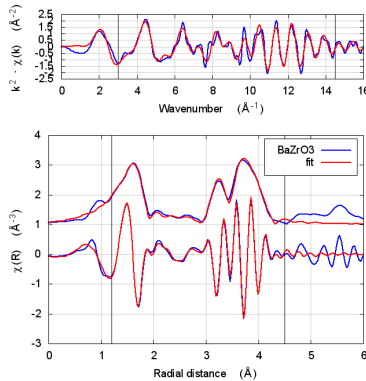
SCF, R=5



SCF, R=5.5



SCF, R=6



## 6.5 Discussion

In the paper cited above, the authors speculate that inaccuracies in FEFF's potential model can be accommodated by allowing separate  $E_0$  parameters to float for each kind of scatterer. In the paper, the claim is that the  $\Delta R$  parameters used to model low temperature BaZrO<sub>3</sub> data correctly follow the trends seen in high temperature XRD data on the same material.

We didn't quite use the same fitting model as in that paper. Instead of a variety of  $\Delta R$

parameters, we use a single isotropic expansion coefficient,  $\alpha$ . With just one data set, the fit using many  $\Delta R$  parameters was not stable.

The hope, in this case, is that self-consistency and charge transfer would make all the  $E_0$  parameters close to 0 **and** remove the need for multiple  $E_0$  parameters in the fit. Neither of those hopes were realized. The  $E_0$  parameters in the self-consistent fits were not much different from the results of the FEFF6 fit and none of them ended up near 0.

Other fitting parameters were, as in other materials, consistent within uncertainties. In this case, the reduced  $\chi^2$  and R-factor were a bit lower with self-consistency with relative reductions on the same scale as the increases in FeS<sub>2</sub> and NiO.

## 7 Bromoadamantane

The data are 1-bromoadamantane. Bromoadamantane is a cycloalkane, meaning that it is a hydrocarbon with rings of carbon atoms. It is also a diamondoid, meaning that it is a strong, stiff, 3D network of covalent bonds. 1-bromoadamantane has one hydrogen atom replaced by a bromine atom.

The material was supplied by Alessandra Leri of Manhattan Marymount College in the form of a white powder. This powder was spread onto Kapton tape which was folded to make a sample with an edge step of about 1.7. The data were measured by Bruce at NSLS beamline X23A2.

This is an interesting test case because it is a molecule (thus the entire molecule can be included in the self-consistency calculation) and because there is measurable scattering from the neighboring hydrogen atoms. While the  $\sigma^2$  of the hydrogen scatterers is not well-determined, the fit is statistically significantly worse when the hydrogen scatterers are excluded.

The fit includes the nearest neighbor C, the next three C atoms, and the neighboring 6 hydrogen atoms. The DS triangle paths involving the first and second neighbor C atoms are also included.

$\Delta R$  parameters are floated for the nearest neighbor carbon, the second neighbor carbon, and the hydrogen scatterers. The adamantane anion is taken to be quite rigid compared to the Br-C bond, so the second neighbor  $\sigma^2$  parameter is constrained to scale geometrically (i.e. by the square of the ratio of the fitted distances) from the  $\sigma^2$  for the nearest neighbor.

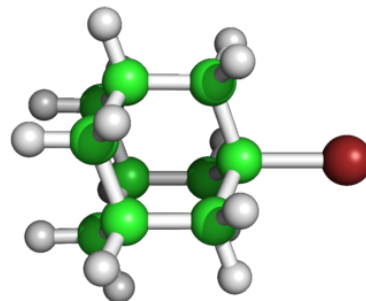


Figure 3: 1-bromoadamantane

### 7.1 Best fit values

model	amp	delr	drc	drh	enot	ss	ssh
feff6	1.35(18)	0.018(11)	-0.013(17)	0.031(22)	5.66(1.39)	0.00522(144)	0.00294(327)
noSCF	1.11(13)	0.014(12)	-0.021(19)	0.076(24)	10.97(1.37)	0.00405(137)	0.00145(326)
withSCF(8)	1.20(12)	0.014(10)	-0.017(15)	0.070(24)	0.57(1.20)	0.00431(119)	0.00363(370)

### 7.2 Statistics

model	$\chi^2$	reduced $\chi^2$	R-factor
feff6	3928	938	0.010
noSCF	4656	1112	0.012
withSCF(8)	3516	839	0.009

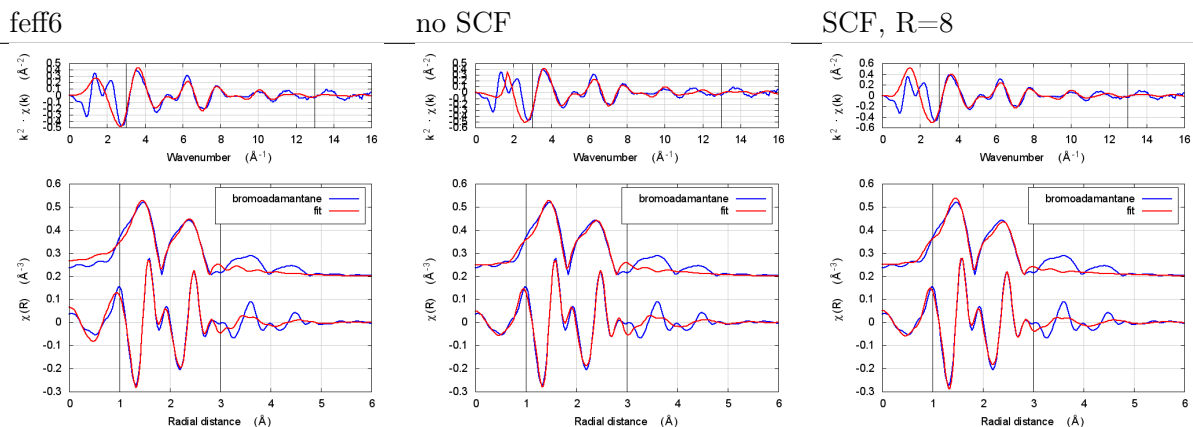
### 7.3 Charge transfer and threshold energy

ip	R=8
0	0.468
1	0.024
2	-0.047
$\mu$	-6.087

Starting value for  $\mu$  in FEFF8 = 4.480

Value for  $\mu$  in FEFF6 = -2.673

## 7.4 Fits



## 7.5 Discussion

In June 2015, the [following quote](#) appeared on the [IFEFFIT mailing list](#):

There are some demonstrated cases where Feff8 is slightly better than Feff6 at modeling EXAFS. The most notable cases are when H is in the input file -- Feff6 is terrible at this.

Bromoadamantane is a case where scattering from H atoms can be seen in the EXAFS data. The statistical parameters are all much smaller when the H SS path is included in the fit compared to fits which exclude that scattering path. This is true even though the  $\sigma^2$  value for the H SS path is ill-determined – its uncertainty is such that  $\sigma^2$  for H is not positive-definite. This is likely because the small mass of the H atom makes its partial pair distribution function highly non-Gaussian. The approximation of a simple  $\sigma^2$  to model this distribution is not all that good. Despite the ill-defined  $\sigma^2$ , the  $\Delta R$  is well defined.

The parameters of the first shell C scatterer are quite well defined and consistent across theory models.  $S_0^2$  varies to the limit of its uncertainty and  $\Delta R$  for the H atom varies outside its uncertainty. The statistical parameters for the fits with self-consistency and FEFF6 are basically indistinguishable.

So, is FEFF6 “terrible” at handling H scatterers? The answer may be “yes” and may be “no”, but these data on bromoadamantane don’t suggest that it is any worse than FEFF8.



## 8 Uranyl hydrate

The data are the hydrated uranyl hydrate shown in DOI: [10.1016/S0016-7037\(02\)00947-X](https://doi.org/10.1016/S0016-7037(02)00947-X)

This is an interesting test case because it involves very short  $\simeq 1.78 \text{ \AA}$  oxygenyl bonds in an  $f$ -electron system.

The AFOLP card was used to run FEFF6. The FOLP card with a value of 0.9 for each potential was used to get FEFF8.5 to run to completion.

Following the lead of that paper, FEFF was run on the crystal sodium uranyl triacetate. The relevant bit of the structure is shown in the figure. For the fitting model, scattering paths related to the axial and equatorial O atoms (red balls) are used in the fit. Other paths are unused. The parameterization given in Tables 2 and 5 is used in this fit.

There is an  $S_0^2$  (`amp`) and an energy shift (`enot`). The axial and equatorial oxygen atoms each get a  $\Delta R$  (`deloax` and `deloeq`) and a  $\sigma^2$  (`sigoax` and `sigoeq`).

`amp` is unitless. `enot` is eV. `deloax` and `deloeq` are  $\text{\AA}$ . `sigoax` and `sigoeq` are  $\text{\AA}^2$ .

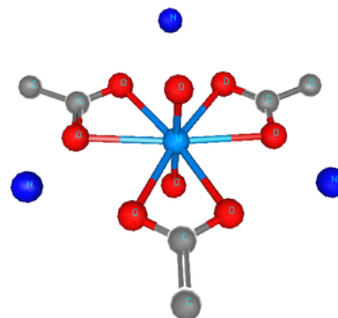


Figure 4: The uranyl motif from sodium uranyl triacetate.

### 8.1 Best fit values

model	amp	deloax	deloeq	enot	sigoax	sigoeq
feff6	0.93(4)	0.03504(396)	-0.04278(770)	10.63(60)	-0.00007(53)	0.00726(94)
noSCF	1.04(6)	0.03684(523)	-0.05319(975)	11.32(78)	0.00032(72)	0.00699(118)
withSCF(2.5)	1.08(6)	0.04165(548)	-0.04475(972)	3.45(81)	0.00074(73)	0.00692(115)
withSCF(2.9)	1.08(6)	0.04172(547)	-0.04485(971)	3.50(81)	0.00074(73)	0.00691(115)
withSCF(4.0)	1.08(6)	0.04144(545)	-0.04455(969)	3.59(81)	0.00075(73)	0.00694(115)
withSCF(5.2)	1.08(6)	0.04154(545)	-0.04473(967)	3.66(81)	0.00074(72)	0.00693(114)
withSCF(6.8)	1.08(6)	0.04163(545)	-0.04478(968)	3.63(81)	0.00074(72)	0.00693(114)

### 8.2 Statistics

model	$\chi^2$	reduced $\chi^2$	R-factor
feff6	37.6972	6.0758	0.0027
noSCF	69.0909	11.1356	0.0049
withSCF(2.5)	71.0295	11.4480	0.0050
withSCF(2.9)	70.8922	11.4259	0.0050
withSCF(4.0)	70.4038	11.3472	0.0050
withSCF(5.2)	70.2351	11.3200	0.0050
withSCF(6.8)	70.3644	11.3408	0.0050

### 8.3 Charge transfer and threshold energy

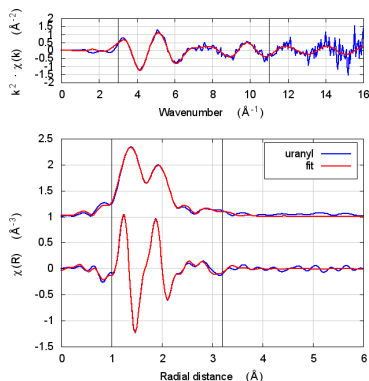
ip	R=2.5	R=2.9	R=4.0	R=5.2	R=6.8
0	1.496	1.487	1.464	1.474	1.467
1	-0.590	-0.582	-0.620	-0.639	-0.633
2	-1.585	-1.600	-1.527	-1.542	-1.546
3	-0.325	-0.329	-0.292	-0.303	-0.310
4	-0.160	-0.154	-0.173	-0.168	-0.168
5	0.628	0.625	0.626	0.630	0.632
$\mu$	-2.810	-2.751	-2.629	-2.569	-2.587

Starting value for  $\mu$  in FEFF8 = 6.030

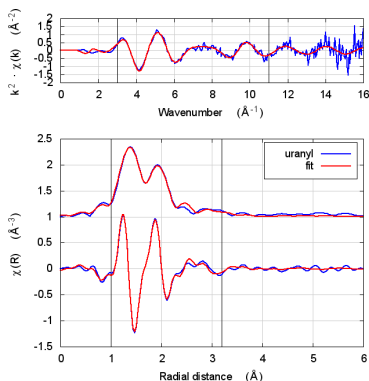
Value for  $\mu$  in FEFF6 = -1.961

## 8.4 Fits

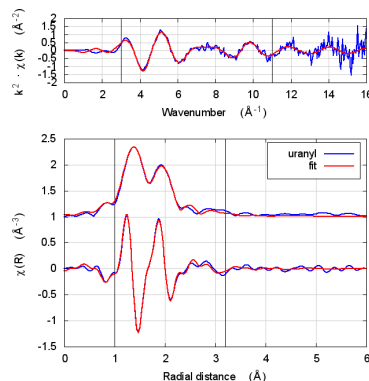
feff6



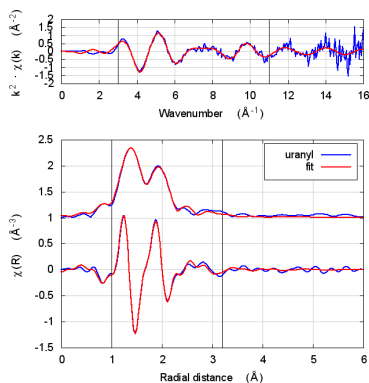
no SCF



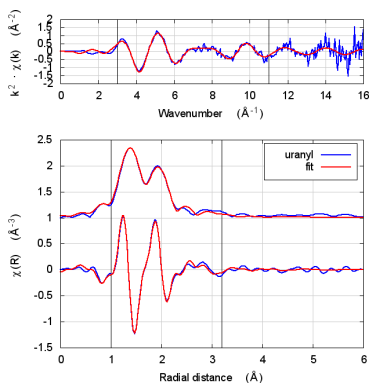
SCF, R=2.5



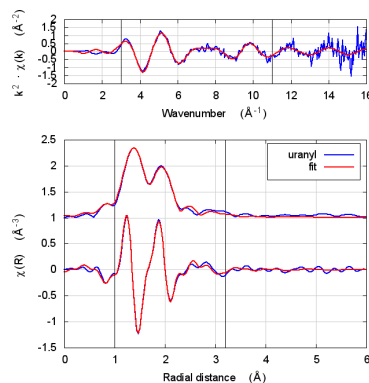
SCF, R=2.9



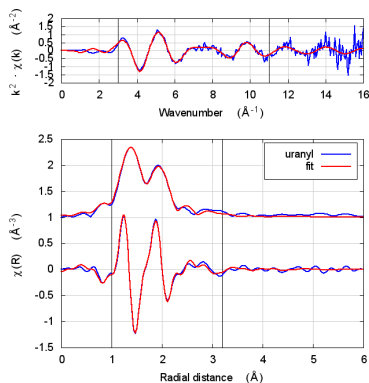
SCF, R=4.0



SCF, R=5.2



SCF, R=6.8



## 8.5 Discussion

The most interesting part of this fit is the extremely short, double bonded, axial oxygen scattering path. With such an extremely rigid bond,  $\sigma^2$  is hard to determine. Even the most sensible result in the table above gives an answer that is barely positive-definite.

Beyond that parameter, the story here is, by now, familiar. Most fitting parameters are consistent over the theory models. This is one of the cases where the statistical parameters are slightly

better for FEFF6 than for any of the FEFF8 fits.

Like with  $\text{UO}_2$ , the  $E_0$  values of the self-consistent fits are what one hopes to find. They are much closer to zero when the edge energy of the data is chosen at the inflection point of the rising edge. Is this a trend suggesting that self-consistency is important for setting the energy scale of  $f$ -electron systems?

Also like the  $\text{UO}_2$  example, the  $S_0^2$  value is a bit different using FEFF6 and FEFF8, which could have an impact on the interpretation of the data. It is, however, correlated with the axial  $\sigma^2$  result.

## 9 Conclusion

Sometimes (FeS<sub>2</sub>, uranyl) the statistical parameters suggest the best fit was found using FEFF6. Sometimes (BaZrO<sub>3</sub>) FEFF8 with self-consistency gave the smaller reduced  $\chi^2$  and R-factor. And sometimes (UO<sub>2</sub>) it made no difference.

Excepting  $E_0$  parameters, the fits presented here yielded equivalent values for fitting parameters using FEFF6 and FEFF8 with self-consistency. Only in the case of  $f$ -electron systems – UO<sub>2</sub> and uranyl – were the fitting results for  $E_0$  parameters more sensible with FEFF8 and self-consistency.

In most cases, the fit using FEFF8 without self-consistency resulted in the largest statistical parameters.

ARTEMIS has used FEFF6 for years. Nothing presented here suggests that was a bad idea.

In the future, ARTEMIS will likely use FEFF85L. It seems that the most sensible default behavior for ARTEMIS would be to run FEFF85L using a very short self-consistency radius.

Is a reviewer justified in demanding that an author use a more recent version of FEFF than FEFF6? On the basis of this presentation here, it seems not.

### 9.1 Theoretical approximations and measurement uncertainty

The most valuable result of this effort – beyond the immediate question of the impact of self-consistent potentials on EXAFS analysis – is that these results provide a sense of what level of uncertainty is introduced to the application of Gaussian statistics to EXAFS analysis by uncertainties in the theory model used as the basis of the fitting.

This paper attempts to quantify many of the sources of uncertainty in an EXAFS measurement. The sort of comparison presented here offers hope of quantifying the contribution to the uncertainty budget of the measurement due to the approximations that enter into the theory.

### 9.2 Interpreting the $E_0$ shift parameter

Way back in the early 1990s, in the days of FEFF3, the theory was already good enough to get calculated, relative peak positions very consistent with experimental data in the EXAFS region. That is, the phase part of the calculation was already highly reliable for large photoelectron kinetic energies in the very earliest days of EXAFS theory.

Consider this paper on a leading contender for the best theoretical approach to XANES and XES, the Bethe-Salpeter equation of motion of the electron-hole pair. This is an impressive and successful approach to core-shell theory, however the positions of peaks in the density of states near the edge, both above and below, are clearly lacking. Consider the MgO calculation in Fig. 5 of that paper. It's a great result, but the peaks are demonstrably shifted relative to experiment.

In the context of finding the threshold energy and the zero of photoelectron wavenumber, a misplacement of peaks in the DOS will result in a misplacement of the threshold. From the FEFF3 results, we know that an  $E_0$  shift is adequate to position the high kinetic energy peaks well with respect to the data. Given the shortcomings even of the current most advanced theory with respect to finding the absolute energy threshold, it is clear that a parameter for an overall  $E_0$  shift remains necessary to line up the EXAFS data with the EXAFS theory. While one must remain mindful that fitted  $E_0$  shifts can be too large, thus confounding the measurement of other parameters, EXAFS analysis continues to require  $E_0$  shift parameters.

### 9.3 A note on the set of standards

For anyone doing EXAFS analysis, a fairly common moment is the one when a fit is not going well, the parameters don't make sense, the fitted function doesn't look like the data, and the person doing the analysis is deeply confused. In that moment, it is extremely tempting to blame the theory.

The truth is, that moment of confusion usually happens with a real research project and typically with a material for which the experimenter has rather little prior knowledge about the actual structure of the sample. While it is tempting to attribute a poor fit to an inadequacy of the theory, it is vastly more likely that the problem is a shortcoming of the fitting model.

In this exercise, we chose a set of materials for which we have excellent prior knowledge about the local configuration around the absorber. With a good structural model, any shortcomings of the fit would then more likely be attributable to shortcomings of the theory.

This exercise, along with long experience, tell us that rather than blame EXAFS theory you should think deeply about your sample and how you represent its structure in the fit. It is much more likely that your sample is something other than what you expect and that the solution to your problem is to prepare a better sample or to dream up a more representative fitting model.