Magnetic Exchange and Valence Delocalization in a Mixed Valence $[Fe^{2+}Fe^{3+}Te_2]^+$ Complex: Insights from Theory and Interpretations of Magnetic and Spectroscopic Data

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Electronic Supporting Information

Starting geometry: model complex 3' with coordinate orientation as shown in Figure 6:

*xyz -1 10

26	0.000000000	0.000000000	-1.583420700
26	0.000000000	0.000000000	1.583420700
52	0.000000400	-2.017263700	0.006754900
52	0.000000400	2.017263300	-0.006754700
7	-1.473721300	-0.076011300	-3.021501000
6	-1.266211300	-0.552668500	-4.242693700
6	-0.005528300	-0.882294000	-4.756160600
1	-0.005515000	-1.397431100	-5.554832100
6	1.258228400	-0.548790700	-4.243286900
7	1.470409200	-0.047753900	-3.028238100
7	1.473722100	0.076010900	3.021501300
6	1.266212200	0.552668100	4.242693900
6	0.005529700	0.882294100	4.756159500
1	0.005515000	1.397431100	5.554832100
6	-1.258227500	0.548790200	4.243287200
7	-1.470409200	0.047753900	3.028238100
6	-2.807147300	0.493994300	-2.791488800
1	-2.883670700	0.868519400	-1.761458900
1	-2.992699100	1.346894800	-3.465420700
1	-3.601774000	-0.254382800	-2.958077500
6	2.835994100	0.419045300	-2.772867600
1	3.371132200	0.629896400	-3.713205500

```
1       2.812876000     1.339204200    -2.170777300
1       3.414979600    -0.338158600    -2.215567700
1       2.128434700    -0.702705800    -4.898389600
1      -2.138491700    -0.708201700    -4.896342400
6      -2.835334100    -0.421125100     2.773458700
1      -3.370638100    -0.630180200     3.714114800
1      -3.415411200     0.333477500     2.213777900
1      -2.810704400    -1.343004100     2.174024400
1      -2.128464600     0.702628900     4.898372000
1       2.138425700     0.708061400     4.896461500
6       2.807455200    -0.493221300     2.791316300
1       2.882857700    -0.870438200     1.762185900
1       3.601470800     0.256552600     2.954527700
1       2.995077100    -1.343990400     3.467364300
*
```

1) A CASSCF calculation for the S=9/2 state using a small artificial shift of 0.01 Å of the two bridging Te2- ligands from left to right along with the "actorbs locorbs" command allows to localize the extra electron on Fe1 thus creating a proper Fe1(d6)Fe(d5) initial guess of orbitals; five 3d orbitals of Fe1(d6) should be on the left, five 3d orbitals should be on the right, Fe(d5); otherwise rotate using the "%scf rotate {126,134,90}… end end" command, along with "maxiter 1", "actorbs unchanged" and "!keepfock"

"asym.inp":

```
!CASSCF DKH-Def2-TZVP  AutoAux DKH2 PAL16  allowrhf  notrah
!nomulliken noloewdin
%scf
maxcore 9000
end

%basis
newgto Te "old-DKH-TZVP" end
end

%rel
method DKH
PictureChange 2
order 2
end

!keepfock # keeps the Fock matrix computed using natural orbitals within the CAS(11,10) active space
```

```
%casscf
nel 11
norb 10
mult 10
nroots 5
actorbs locorbs
trafostep rimo
maxiter 300
end

*xyz -1 10
26      0.000000000     0.000000000    -1.583420700
26      0.000000000     0.000000000     1.583420700
52      0.000000400    -2.017263700     0.016754900
52      0.000000400     2.017263300     0.016754700
7      -1.473721300    -0.076011300    -3.021501000
6      -1.266211300    -0.552668500    -4.242693700
6      -0.005528300    -0.882294000    -4.756160600
1      -0.005515000    -1.397431100    -5.554832100
6       1.258228400    -0.548790700    -4.243286900
7       1.470409200    -0.047753900    -3.028238100
7       1.473722100     0.076010900     3.021501300
6       1.266212200     0.552668100     4.242693900
```

This produce an “asym.gbw” file.

2) The calculation is now being repeated by reading the “asym.gbw” using the initial non-distorted structure;

The “asym.gbw” file computed with the distorted geometry is being accepted when using the non-distorted one.

“sym.inp”:

```
!CASSCF DKH-Def2-TZVP  AutoAux DKH2 PAL16  allowrhf  notrah
!nomulliken noloewdin
!moread
%moinp "asym.gbw"


%scf
maxcore 9000
end
```

```
%basis
newgto Te "old-DKH-TZVP" end
end

%rel
method DKH
PictureChange 2
order 2
end

!keepfock

%casscf
nel 11
norb 10
mult 10
nroots 5
actorbs locorbs
trafostep rimo
maxiter 300
end
*xyz -1 10
26       0.000000000     0.000000000    -1.583420700
26       0.000000000     0.000000000     1.583420700
52       0.000000400    -2.017263700     0.006754900
52       0.000000400     2.017263300    -0.006754700
7       -1.473721300    -0.076011300    -3.021501000
6       -1.266211300    -0.552668500    -4.242693700
6       -0.005528300    -0.882294000    -4.756160600
1       -0.005515000    -1.397431100    -5.554832100
6        1.258228400    -0.548790700    -4.243286900
7        1.470409200    -0.047753900    -3.028238100
7        1.473722100     0.076010900     3.021501300
6        1.266212200     0.552668100     4.242693900
6        0.005529700     0.882294100     4.756159500
1        0.005515000     1.397431100     5.554832100
6       -1.258227500     0.548790200     4.243287200
```

7	-1.470409200	0.047753900	3.028238100
6	-2.807147300	0.493994300	-2.791488800
1	-2.883670700	0.868519400	-1.761458900
1	-2.992699100	1.346894800	-3.465420700
1	-3.601774000	-0.254382800	-2.958077500
6	2.835994100	0.419045300	-2.772867600
1	3.371132200	0.629896400	-3.713205500
1	2.812876000	1.339204200	-2.170777300
1	3.414979600	-0.338158600	-2.215567700
1	2.128434700	-0.702705800	-4.898389600
1	-2.138491700	-0.708201700	-4.896342400
6	-2.835334100	-0.421125100	2.773458700
1	-3.370638100	-0.630180200	3.714114800

1	-3.415411200	0.333477500	2.213777900
1	-2.810704400	-1.343004100	2.174024400
1	-2.128464600	0.702628900	4.898372000
1	2.138425700	0.708061400	4.896461500
6	2.807455200	-0.493221300	2.791316300
1	2.882857700	-0.870438200	1.762185900
1	3.601470800	0.256552600	2.954527700
1	2.995077100	-1.343990400	3.467364300

*

3) “cp sym.fsv sym2.fsv”; “cp sym.gbw sym2.gbw” – this is just to avoid overwriting “sym.gbw”

The command “orca_blockf sym2.fsv sym2.gbw 126 130 131 135” is used to produce a very compact form of the Fock matrix which speeds up all following calculations by a factor of two; orca_blockf reads the 10x10 Fock matrix and diagonalizes the sub-blocks 126 to 130 for FeII(d6) and 131 to 135 for FeIII(d5). It then overwrites the sym.gbw file with the new Fock orbitals – the eigenvectors of each block. Upon execution the following information is given at the screen(“orca_blockf sym.fsv sym.gbw 126 130 131 135 >file.txt” would save it in a file).

Fock matrix file: sym4.fsv

GBW file : sym4.gbw

Block 0 = 126 to 130

Block 1 = 131 to 135

Successfully read the orbitals matrix of dimension 810

Successfully read the Fock matrix of dimension 810

Starting block diagonalization:

Local Fock Matrix

	0	1	2	3	4
0	-0.033802	0.011017	-0.001565	0.003796	0.000937

1	0.011017	-0.035832	-0.003448	0.004698	-0.000817
2	-0.001565	-0.003448	-0.033682	-0.010365	0.000896
3	0.003796	0.004698	-0.010365	-0.036396	0.001074
4	0.000937	-0.000817	0.000896	0.001074	-0.038011

Local Eigenvectors

	0	1	2	3	4
0	0.652878	0.012009	0.053593	-0.555942	0.511530
1	-0.731277	0.145256	-0.143108	-0.389880	0.521199
2	-0.146075	-0.609748	0.073352	-0.613818	-0.474042
3	-0.042919	-0.756955	0.151460	0.400403	0.491848
4	-0.125717	0.184344	0.973821	-0.042739	0.007650

Local Eigenvalues (eV)

0	-1.257744
1	-1.250866
2	-1.023289
3	-0.829020
4	-0.475170

Local Fock Matrix

	0	1	2	3	4
0	-0.170620	0.001854	0.002583	0.000789	0.016022
1	0.001854	-0.165866	-0.001708	-0.001624	-0.001475
2	0.002583	-0.001708	-0.170027	-0.016406	-0.000073
3	0.000789	-0.001624	-0.016406	-0.166890	-0.000298
4	0.016022	-0.001475	-0.000073	-0.000298	-0.166678

Local Eigenvectors

	0	1	2	3	4
0	0.531958	-0.519115	0.083613	-0.516270	0.417150
1	-0.153105	0.004219	0.988170	0.003653	0.006946
2	-0.537569	-0.500678	-0.086458	0.382762	0.553498
3	-0.468363	-0.477473	-0.064775	-0.473254	-0.569640
4	-0.430390	0.501839	-0.069704	-0.602475	0.441688

Local Eigenvalues (eV)

0	-5.100016
1	-4.977158
2	-4.499366
3	-4.166790
4	-4.116405

Writing GBW file sym.gbw

.... all done ... leaving gracefully

4) Inputs for the state specific CASSCF/NEVPT2 calculations of the S=1/2, S=3/2, S=5/2, S=7/2 and S=9/2 spin-ladder states, please notice the request of computing two roots for each ladder spin.

S=1/2; "1over22roots.inp"

```
!CASSCF DKH-Def2-TZVP  AutoAux DKH2 PAL16 ri-jk conv tightscf  notrah

!xyzfile normalprint

!nevpt2

!moread

%moinp "sym2.gbw"


! somf(1x)


%cpcm

surfacetype vdw_gaussian

num_leb 302

end


%scf

maxcore 9000

end


%scf

maxiter 300

end


%basis

newgto Te "old-DKH-TZVP" end

end


%rel

method DKH

PictureChange 2

order 2

end
```

```
!keepfock

%casscf
nel 11
norb 10
mult 2
nroots 2
actorbs unchanged
actconstraints 1
printgstate 1
ptsettings
  d4tpre 1e-14
end
ci
maxiter 300
nguessmat 4500
end
trafostep rimo
end

*xyz -1 10
26      0.000000000     0.000000000    -1.583420700
26      0.000000000     0.000000000     1.583420700
52      0.000000400    -2.017263700     0.006754900
52      0.000000400     2.017263300    -0.006754700
7      -1.473721300    -0.076011300    -3.021501000
6      -1.266211300    -0.552668500    -4.242693700
6      -0.005528300    -0.882294000    -4.756160600
1       0.005515000     1.397431100     5.554832100
6      -1.258227500     0.548790200     4.243287200
7      -1.470409200     0.047753900     3.028238100
6      -2.807147300     0.493994300    -2.791488800
1      -2.883670700     0.868519400    -1.761458900
1      -2.992699100     1.346894800    -3.465420700
1      -3.601774000    -0.254382800    -2.958077500
6       2.835994100     0.419045300    -2.772867600
1       3.371132200     0.629896400    -3.713205500
1       2.812876000     1.339204200    -2.170777300
```

1 3.414979600 -0.338158600 -2.215567700

1 2.128434700 -0.702705800 -4.898389600

1 -2.138491700 -0.708201700 -4.896342400

6 -2.835334100 -0.421125100 2.773458700

1 -3.370638100 -0.630180200 3.714114800

1 -3.415411200 0.333477500 2.213777900

1 -2.810704400 -1.343004100 2.174024400

1 -2.128464600 0.702628900 4.898372000

1 2.138425700 0.708061400 4.896461500

6 2.807455200 -0.493221300 2.791316300

1 2.882857700 -0.870438200 1.762185900

1 3.601470800 0.256552600 2.954527700

1 2.995077100 -1.343990400 3.467364300

*

Input files for S=3/2, 5/2, 7/2 and 9/2 are generated by just replacing the “mult 2” keyword by 4,6,8 and 10, respectively.

Nummerical results for total CASSCF and CASSCF/NEVPT2 energies are collected in the Table below.

Spin S	CASSCF	CASSCF/NEVPT2	Timing PAL16
1/2	-16727.95407159654496 -16727.95331723532217	-16731.74399761719178 -16731.74413249810823	2 hours 41 minutes
3/2	-16727.95370539729265 -16727.95300107157891	-16731.74305280171029 -16731.74325040547046	2 hours 54 minutes
5/2	-16727.95313078911568 -16727.95251541185644	-16731.74160971988022 -16731.74192477801626	54 minutes
7/2	-16727.95239625727845 -16727.95191527828865	-16731.73984355355424 -16731.74033972478719	57 minutes
9/2	-16727.95156451025105 -16727.95126441148750	-16731.73799803745351 -16731.73867055172741	55 minutes

These have been utilized in the following sample MatLab script yielding best fit J and J’ values and standard deviations in Table 4, “State specific CASSCF, CASSCF/NEVPT2 columns. In the same way other entries of Table 4 have been computed.

MatLab script: fe2te2jj1suppinf.m

```
clear all
clc
% % % CAS(11,10) state specific, CASSCF
% %
% %
eref=[
% S=1/2
-16727.95407159654496  -16727.95331723532217
% S=3/2
-16727.95370539729265  -16727.95300107157891
% S=5/2
-16727.95313078911568  -16727.95251541185644
% S=7/2
-16727.95239625727845  -16727.95191527828865
```

```
% S=9/2
-16727.95156451025105  -16727.95126441148750
];

% % % CAS(11,10) state specific, CASSCF+NEVPT2
% %
% %
% eref=[
% % S=1/2
%  -16731.74399761719178  -16731.74413249810823
% % S=3/2
% -16731.74305280171029    -16731.74325040547046
% % S=5/2
% -16731.74160971988022    -16731.74192477801626
% % S=7/2
% -16731.73984355355424    -16731.74033972478719
% % S=9/2
% -16731.73799803745351    -16731.73867055172741
% ];




eref2=(eref(:,1)+eref(:,2))/2;
eref2=(eref2-eref2(1,1))*8065*27.211;
eref22=eref2-eref2(5)

%
S=[1/2  3/2   5/2   7/2  9/2]
bparameters(5)=zeros;
for i=1:5
bparameters(i)=((eref(i,2)-eref(i,1))/2*8065*27.211/(S(i)+1/2));
end

bparameters



% fit to an isotropic non-Heisenberg exchange hamiltonian:
% -2Jab(Sa*Sb)-2J1ab*(Sa*Sb)^2
% with the Heisenberg exchange (the first term) and the biquadratic
% exchange (the second term)
A(5,2)=zeros;
for i=1:5
A(i,1)=-S(i)*(S(i)+1);
A(i,2)=-(S(i)*(S(i)+1))^2;
end

B(4,2)=zeros;
A(1:5,:)=A(1:5,:)-A(1,:);
B(1,:)=A(2,:);
B(2,:)=A(3,:);
B(3,:)=A(4,:);
B(4,:)=A(5,:);
Y(1,1)=eref2(2,1);
Y(2,1)=eref2(3,1);
```

```
Y(3,1)=eref2(4,1);
Y(4,1)=eref2(5,1);
eref2

% Y(1,1)=data6(1,1);
% Y(2,1)=data6(2,1);
% Y(3,1)=data6(3,1);
% Y(4,1)=data6(4,1);

% B*X=Y; X=pinv(B)*Y;
% Heisenberg pljus Biqadratic
% X(1)=Jab; X(2)=Jab'
X=pinv(B)*Y
Ycalc=B*X;
plot(Y,Ycalc,'o')
compar=[Y  Ycalc]
diff=Y-Ycalc
stand_dev=sqrt(diff'*diff/3)
plot(Y,Ycalc,'o')
```

5.Input files for calculation of the spin-orbit coupling multiplets (Table 5).

Computations of multiplet fine structures inevitably requires account of spin-orbit coupling. In this work it is taken into account using quasidegenerate perturbation theory within the scalar relativistic basis, best using the entire Hilbert space of a given spin. Here we used the lowest 40 scalar relativistic eigenfunctions and energy eigenvalues which yields a correct reproduction of the fine structure of the lowest spin. The following input was used to generate a proper well-balanced description of scalar relativistic eigenvalues which treats different spin energy levels on equal footing. Each local S=2 FeII(d6) state couples to the S=5/2 ground state of FeIII(d5) to yield S=1/2, 3/2, 5/2, 7/2 and 9/2 pair state. Since there are five S=2 states of FeII(d6) this results in five scalar relativistic roots for each ladder spin.

"5roots.inp":

```
!CASSCF DKH-Def2-TZVP  AutoAux DKH2 PAL16 ri-jk conv tightscf  notrah

!xyzfile normalprint

!nevpt2

!moread

%moinp "sym2.gbw"


! somf(1x)


%cpcm

surfacetype vdw_gaussian

num_leb 302

end


%scf

maxcore 9000

end


%scf
```

```
maxiter 300
end

%basis
newgto Te "old-DKH-TZVP" end
end

%rel
method DKH
PictureChange 2
order 2
end

!keepfock
%casscf
nel 11
norb 10
mult 10,8,6,4,2
nroots 5,5,5,5,5
actorbs unchanged
actconstraints 1
printgstate 1
ptsettings
  d4tpre 1e-14
end
ci
maxiter 300
nguessmat 4500
end
trafostep rimo
end

*xyz -1 10
26      0.000000000     0.000000000    -1.583420700
26      0.000000000     0.000000000     1.583420700
52      0.000000400    -2.017263700     0.006754900
52      0.000000400     2.017263300    -0.006754700
7      -1.473721300    -0.076011300    -3.021501000
```

```
6    -1.266211300   -0.552668500   -4.242693700
6    -0.005528300   -0.882294000   -4.756160600
1    -0.005515000   -1.397431100   -5.554832100
6     1.258228400   -0.548790700   -4.243286900
7     1.470409200   -0.047753900   -3.028238100
7     1.473722100    0.076010900    3.021501300
6     1.266212200    0.552668100    4.242693900
6     0.005529700    0.882294100    4.756159500
1     0.005515000    1.397431100    5.554832100
6    -1.258227500    0.548790200    4.243287200
7    -1.470409200    0.047753900    3.028238100
6    -2.807147300    0.493994300   -2.791488800
1    -2.883670700    0.868519400   -1.761458900
1    -2.992699100    1.346894800   -3.465420700
1    -3.601774000   -0.254382800   -2.958077500
6     2.835994100    0.419045300   -2.772867600
1     3.371132200    0.629896400   -3.713205500
1     2.812876000    1.339204200   -2.170777300
1     3.414979600   -0.338158600   -2.215567700
1     2.128434700   -0.702705800   -4.898389600
1    -2.138491700   -0.708201700   -4.896342400
6    -2.835334100   -0.421125100    2.773458700
1    -3.370638100   -0.630180200    3.714114800
1    -3.415411200    0.333477500    2.213777900
1    -2.810704400   -1.343004100    2.174024400
1    -2.128464600    0.702628900    4.898372000
1     2.138425700    0.708061400    4.896461500
6     2.807455200   -0.493221300    2.791316300
1     2.882857700   -0.870438200    1.762185900
1     3.601470800    0.256552600    2.954527700
1     2.995077100   -1.343990400    3.467364300
*
```

This calculation yields a 5roots.gbw file which provides proper initial guess for the calculation of the fine structure of the S=1/2, 3/2, 5/2, 7/2 and 9/2 ground states. Here we list the input file for the calculation of the S=3/2 ground state Kramer's quartet. "s3over240roots.inp":

```
!CASSCF DKH-Def2-TZVP  AutoAux DKH2 PAL16 ri-jk conv tightscf  notrah
!xyzfile normalprint
!nevpt2
```

```
!moread
%moinp "5roots.gbw"

! somf(1x)

%cpcm
surfacetype vdw_gaussian
num_leb 302
end

%scf
maxcore 9000
end

%scf
maxiter 300
end

%basis
newgto Te "old-DKH-TZVP" end
end

%rel
method DKH
PictureChange 2
order 2
end


!keepfock

%casscf
nel 11
norb 10
mult 4
nroots 40
actorbs unchanged
actconstraints 1
```

```
maxiter 1
printgstate 1
ptsettings
  d4tpre 1e-14
end
ci
maxiter 300
nguessmat 4500
end
trafostep rimo
rel
dosoc true
gtensor true
printlevel 3
NDoubGTensor 16
 domagnetization true
 dosusceptibility true
 nPointsFStep 5
 MAGFieldStep 100.0
MAGTemperatureMIN 0
 MAGTemperatureMAX 3
 MAGTemperatureNPoints 100
 MAGFieldMIN 70000.0
 MAGFieldMAX 10000.0
 MAGNpoints 3
 SUSTempMIN 0
 SUSTempMAX 200.0
 SUSNPoints 150
 SUSStatFieldMIN 10000.0
 SUSStatFieldMAX 10000.0
 SUSStatFieldNPoints 1
 end
end

*xyz -1 10
26      0.000000000     0.000000000    -1.583420700
26      0.000000000     0.000000000     1.583420700
52      0.000000400    -2.017263700     0.006754900
```

52	0.000000400	2.017263300	-0.006754700
7	-1.473721300	-0.076011300	-3.021501000
6	-1.266211300	-0.552668500	-4.242693700
6	-0.005528300	-0.882294000	-4.756160600
1	-0.005515000	-1.397431100	-5.554832100
6	1.258228400	-0.548790700	-4.243286900
7	1.470409200	-0.047753900	-3.028238100
7	1.473722100	0.076010900	3.021501300
6	1.266212200	0.552668100	4.242693900
6	0.005529700	0.882294100	4.756159500
1	0.005515000	1.397431100	5.554832100
6	-1.258227500	0.548790200	4.243287200
7	-1.470409200	0.047753900	3.028238100
6	-2.807147300	0.493994300	-2.791488800
1	-2.883670700	0.868519400	-1.761458900
1	-2.992699100	1.346894800	-3.465420700
1	-3.601774000	-0.254382800	-2.958077500
6	2.835994100	0.419045300	-2.772867600
1	3.371132200	0.629896400	-3.713205500
1	2.812876000	1.339204200	-2.170777300
1	3.414979600	-0.338158600	-2.215567700
1	2.128434700	-0.702705800	-4.898389600
1	-2.138491700	-0.708201700	-4.896342400
6	-2.835334100	-0.421125100	2.773458700
1	-3.370638100	-0.630180200	3.714114800
1	-3.415411200	0.333477500	2.213777900
1	-2.810704400	-1.343004100	2.174024400
1	-2.128464600	0.702628900	4.898372000
1	2.138425700	0.708061400	4.896461500
6	2.807455200	-0.493221300	2.791316300
1	2.882857700	-0.870438200	1.762185900
1	3.601470800	0.256552600	2.954527700
1	2.995077100	-1.343990400	3.467364300

*

The following remarks concerning this calculation should be done:

i) Using “actorbs unchanged” and “actconstraints 1” is essential, it keeps the localized orbital description, i.e. FeII(d6) left and FeIII(d5) right.

ii) Using “maxiter 1” is essential, i.e. localized orbitals *are not iterated,* keeping a proper balance between roots of different spin-multiplicity, thus allowing to compare fine structures (zero-field splittings (for S>1/2) Kramer’s doublet g-factors.

iii) Extra keywords in the spin-orbit coupling “rel” part of the %casscf block are provided.

iv) "nevpt2" is applied on top of the proper guess orbitals even without casscf convergence ("maxiter 1").

Deducing charge transfer parameters:

At step 3 we did not override the sym.gbw file when block diagonalising the 10x10 local Fock matrix; let us now apply orca_blockf twice as follows:

i) orca_blockf sym.fsv sym.gbw 126 130 131 135

ii) orca_blockf sym.fsv sym.gbw 126 135

The first command was already executed producing block diagonal FeII(d6) and FeIII(d5) matrices

The second command renders the block diagonal for FeII(d6) and FeIII(d5) unaltered by give a 5x5 of diagonal block with charge transfer (hoppin integrals) for the electrons of FeII(d6) from FeII to FeIII:

Local Fock Matrix

	0	1	2	3	4	5
0	-0.046221	0.000000	-0.000000	0.000000	0.000000	-0.000179
1	0.000000	-0.045968	-0.000000	-0.000000	0.000000	0.000975
2	-0.000000	-0.000000	-0.037605	-0.000000	-0.000000	0.003522
3	0.000000	-0.000000	-0.000000	-0.030466	0.000000	-0.003136
4	0.000000	0.000000	-0.000000	0.000000	-0.017462	-0.000069
5	-0.000179	0.000975	0.003522	-0.003136	-0.000069	-0.187422
6	0.008735	0.006468	-0.000350	0.000201	0.000164	0.000000
7	0.005516	-0.007769	-0.025116	0.000845	-0.000107	0.000000
8	0.002807	-0.003946	0.000846	0.021525	0.000470	0.000000
9	0.000480	-0.000403	-0.000191	0.002881	-0.007055	-0.000000

	6	7	8	9
0	0.008735	0.005516	0.002807	0.000480
1	0.006468	-0.007769	-0.003946	-0.000403
2	-0.000350	-0.025116	0.000846	-0.000191
3	0.000201	0.000845	0.021525	0.002881
4	0.000164	-0.000107	0.000470	-0.007055
5	0.000000	0.000000	0.000000	-0.000000
6	-0.182907	-0.000000	-0.000000	-0.000000
7	-0.000000	-0.165349	-0.000000	-0.000000
8	-0.000000	-0.000000	-0.153127	0.000000
9	-0.000000	-0.000000	0.000000	-0.151275

The following MatLab script allows to extract diagonal orbital energies in eV and off-diagonal hopping integrals in cm-1:

```
clear all
clc

data(1:10,1:6)=[-0.046221   0.000000  -0.000000   0.000000   0.000000  -0.000179
             0.000000  -0.045968  -0.000000  -0.000000   0.000000   0.000975
            -0.000000  -0.000000  -0.037605  -0.000000  -0.000000   0.003522
             0.000000  -0.000000  -0.000000  -0.030466   0.000000  -0.003136
             0.000000   0.000000  -0.000000   0.000000  -0.017462  -0.000069
            -0.000179   0.000975   0.003522  -0.003136  -0.000069  -0.187422
             0.008735   0.006468  -0.000350   0.000201   0.000164   0.000000
             0.005516  -0.007769  -0.025116   0.000845  -0.000107   0.000000
             0.002807  -0.003946   0.000846   0.021525   0.000470   0.000000
             0.000480  -0.000403  -0.000191   0.002881  -0.007055  -0.000000];


data(1:10,7:10)=[0.008735   0.005516   0.002807   0.000480
                 0.006468  -0.007769  -0.003946  -0.000403
                -0.000350  -0.025116   0.000846  -0.000191
                 0.000201   0.000845   0.021525   0.002881
                 0.000164  -0.000107   0.000470  -0.007055
                 0.000000   0.000000   0.000000  -0.000000
                -0.182907  -0.000000  -0.000000  -0.000000
                -0.000000  -0.165349  -0.000000  -0.000000
                -0.000000  -0.000000  -0.153127   0.000000
                -0.000000  -0.000000   0.000000  -0.151275];
% diagonal elements in eV
data(1:5,1:5)*27.211
data(6:10,6:10)*27.211
% off-diagonal elements in cm-1
data(1:5,6:10)*27.211*8065
```

It was used to list Table 9.

Electronic structure and magnetic anisotropy of the $Fe^{2+}Te_2N_2$ and $Fe^{3+}Te_2N_2$ building units.

The following input files we used to compute entries listed in Table 2.

$Fe^{2+}Te_2N_2$:fegaguess.inp (getting initial guess):

```
!CASSCF DKH-Def2-TZVP  AutoAux DKH2 PAL16  noiter  notrah
!xyzfile normalprint

! somf(1x)

%cpcm
surfacetype vdw_gaussian
num_leb 302
end

%scf
maxcore 4000
end

%scf
maxiter 300
end

%basis
newgto Te "old-DKH-TZVP" end
end

%rel
method DKH
PictureChange 2
order 2
end

%casscf
nel 6
norb 5
mult 5
nroots 5
orbstep superci
                    switchstep diis
                   shiftup 1
                   shiftdn 1
trafostep rimo
```

end

*xyz -1 5

26	0.000000000	0.000000000	-1.583420700
31	0.000000000	0.000000000	1.583420700
52	0.000000400	-2.017263700	0.006754900
52	0.000000400	2.017263300	-0.006754700
7	-1.473721300	-0.076011300	-3.021501000
6	-1.266211300	-0.552668500	-4.242693700
6	-0.005528300	-0.882294000	-4.756160600
1	-0.005515000	-1.397431100	-5.554832100
6	1.258228400	-0.548790700	-4.243286900
7	1.470409200	-0.047753900	-3.028238100
7	1.473722100	0.076010900	3.021501300
6	1.266212200	0.552668100	4.242693900
6	0.005529700	0.882294100	4.756159500
1	0.005515000	1.397431100	5.554832100
6	-1.258227500	0.548790200	4.243287200
7	-1.470409200	0.047753900	3.028238100
6	-2.807147300	0.493994300	-2.791488800
1	-2.883670700	0.868519400	-1.761458900
1	-2.992699100	1.346894800	-3.465420700
1	-3.601774000	-0.254382800	-2.958077500
6	2.835994100	0.419045300	-2.772867600
1	3.371132200	0.629896400	-3.713205500
1	2.812876000	1.339204200	-2.170777300
1	3.414979600	-0.338158600	-2.215567700
1	2.128434700	-0.702705800	-4.898389600
1	-2.138491700	-0.708201700	-4.896342400
6	-2.835334100	-0.421125100	2.773458700
1	-3.370638100	-0.630180200	3.714114800
1	-3.415411200	0.333477500	2.213777900
1	-2.810704400	-1.343004100	2.174024400
1	-2.128464600	0.702628900	4.898372000
1	2.138425700	0.708061400	4.896461500
6	2.807455200	-0.493221300	2.791316300
1	2.882857700	-0.870438200	1.762185900
1	3.601470800	0.256552600	2.954527700

1 2.995077100 -1.343990400 3.467364300

*

feganev.inp:

!CASSCF DKH-Def2-TZVP AutoAux DKH2 PAL16 notrah

!xyzfile normalprint

!moread

%moinp "fegaguess.gbw"

! somf(1x)

%cpcm

surfacetype vdw_gaussian

num_leb 302

end

%scf

maxcore 4000

end

%scf

maxiter 300

end

%scf rotate {128,133,90} end end

%basis

newgto Te "old-DKH-TZVP" end

end

%rel

method DKH

PictureChange 2

order 2

end

%casscf

nel 6

norb 5

```
mult 5,3
nroots 5,45
orbstep superci
                    switchstep diis
                   shiftup 1
                   shiftdn 1
actorbs dorbs
#nevpt2 true
trafostep rimo
rel
dosoc true
gtensor true
printlevel 3
#NDoubGTensor 3
 domagnetization true
 dosusceptibility true
 nPointsFStep 5
 MAGFieldStep 100.0
 MAGTemperatureMIN 0
 MAGTemperatureMAX 3
 MAGTemperatureNPoints 100
 MAGFieldMIN 70000.0
 MAGFieldMAX 10000.0
 MAGNpoints 3
 SUSTempMIN 0
SUSTempMAX 200.0
 SUSNPoints 150
 SUSStatFieldMIN 10000.0
 SUSStatFieldMAX 10000.0
 SUSStatFieldNPoints 1
 end
end

*xyz -1 5
26      0.000000000     0.000000000    -1.583420700
31      0.000000000     0.000000000     1.583420700
52      0.000000400    -2.017263700     0.006754900
52      0.000000400     2.017263300    -0.006754700
```

7	-1.473721300	-0.076011300	-3.021501000
6	-1.266211300	-0.552668500	-4.242693700
6	-0.005528300	-0.882294000	-4.756160600
1	-0.005515000	-1.397431100	-5.554832100
6	1.258228400	-0.548790700	-4.243286900
7	1.470409200	-0.047753900	-3.028238100
7	1.473722100	0.076010900	3.021501300
6	1.266212200	0.552668100	4.242693900
6	0.005529700	0.882294100	4.756159500
1	0.005515000	1.397431100	5.554832100
6	-1.258227500	0.548790200	4.243287200
7	-1.470409200	0.047753900	3.028238100
6	-2.807147300	0.493994300	-2.791488800
1	-2.883670700	0.868519400	-1.761458900
1	-2.992699100	1.346894800	-3.465420700
1	-3.601774000	-0.254382800	-2.958077500
6	2.835994100	0.419045300	-2.772867600
1	3.371132200	0.629896400	-3.713205500
1	2.812876000	1.339204200	-2.170777300
1	3.414979600	-0.338158600	-2.215567700
1	2.128434700	-0.702705800	-4.898389600
1	-2.138491700	-0.708201700	-4.896342400
6	-2.835334100	-0.421125100	2.773458700
1	-3.370638100	-0.630180200	3.714114800
1	-3.415411200	0.333477500	2.213777900
1	-2.810704400	-1.343004100	2.174024400
1	-2.128464600	0.702628900	4.898372000
1	2.138425700	0.708061400	4.896461500
6	2.807455200	-0.493221300	2.791316300
1	2.882857700	-0.870438200	1.762185900
1	3.601470800	0.256552600	2.954527700
1	2.995077100	-1.343990400	3.467364300

*

$Fe^{3+}Te_2N_2$: feznguess.inp (getting initial guess):

!CASSCF DKH-Def2-TZVP AutoAux DKH2 PAL16 ri-jk conv noiter notrah

!xyzfile normalprint

```
! somf(1x)

%cpcm
surfacetype vdw_gaussian
num_leb 302
end

%scf
maxcore 9000
end

%scf
maxiter 300
end

%basis
newgto Te "old-DKH-TZVP" end
end

%rel
method DKH
PictureChange 2
order 2
end


!keepfock

%casscf
nel 5
norb 5
mult 6,4
nroots 1,24
trafostep rimo
end

*xyz -1 6
```

26	0.000000000	0.000000000	-1.583420700
30	0.000000000	0.000000000	1.583420700
52	0.000000400	-2.017263700	0.006754900
52	0.000000400	2.017263300	-0.006754700
7	-1.473721300	-0.076011300	-3.021501000
6	-1.266211300	-0.552668500	-4.242693700
6	-0.005528300	-0.882294000	-4.756160600
1	-0.005515000	-1.397431100	-5.554832100
6	1.258228400	-0.548790700	-4.243286900
7	1.470409200	-0.047753900	-3.028238100
7	1.473722100	0.076010900	3.021501300
6	1.266212200	0.552668100	4.242693900
6	0.005529700	0.882294100	4.756159500
1	0.005515000	1.397431100	5.554832100
6	-1.258227500	0.548790200	4.243287200
7	-1.470409200	0.047753900	3.028238100
6	-2.807147300	0.493994300	-2.791488800
1	-2.883670700	0.868519400	-1.761458900
1	-2.992699100	1.346894800	-3.465420700
1	-3.601774000	-0.254382800	-2.958077500
6	2.835994100	0.419045300	-2.772867600
1	3.371132200	0.629896400	-3.713205500
1	2.812876000	1.339204200	-2.170777300
1	3.414979600	-0.338158600	-2.215567700
1	2.128434700	-0.702705800	-4.898389600
1	-2.138491700	-0.708201700	-4.896342400
6	-2.835334100	-0.421125100	2.773458700
1	-3.370638100	-0.630180200	3.714114800
1	-3.415411200	0.333477500	2.213777900
1	-2.810704400	-1.343004100	2.174024400
1	-2.128464600	0.702628900	4.898372000
1	2.138425700	0.708061400	4.896461500
6	2.807455200	-0.493221300	2.791316300
1	2.882857700	-0.870438200	1.762185900
1	3.601470800	0.256552600	2.954527700
1	2.995077100	-1.343990400	3.467364300

*

feznnev.inp:

```
!CASSCF DKH-Def2-TZVP  AutoAux DKH2 PAL16 ri-jk conv  notrah
!xyzfile normalprint
!nevpt2
!moread
%moinp "feznguess.gbw"

! somf(1x)

%cpcm
surfacetype vdw_gaussian
num_leb 302
end

%scf
maxcore 9000
end

%scf rotate  {128,131,90} {130,133,90}  end end

%scf
maxiter 300
end

%basis
newgto Te "old-DKH-TZVP" end
end

%rel
method DKH
PictureChange 2
order 2
end

%casscf
nel 5
norb 5
mult 6,4
nroots 1,24
```

```
actorbs dorbs
trafostep rimo
rel
dosoc true
gtensor true
printlevel 3
NDoubGTensor 3
domagnetization true
dosusceptibility true
nPointsFStep 5
MAGFieldStep 100.0
MAGTemperatureMIN 0
MAGTemperatureMAX 3
MAGTemperatureNPoints 100
MAGFieldMIN 70000.0
MAGFieldMAX 10000.0
MAGNpoints 3
SUSTempMIN 0
SUSTempMAX 200.0
SUSNPoints 150
SUSStatFieldMIN 10000.0
SUSStatFieldMAX 10000.0
SUSStatFieldNPoints 1
end
end

*xyz -1 6
26      0.000000000     0.000000000    -1.583420700
30      0.000000000     0.000000000     1.583420700
52      0.000000400    -2.017263700     0.006754900
52      0.000000400     2.017263300    -0.006754700
7      -1.473721300    -0.076011300    -3.021501000
6      -1.266211300    -0.552668500    -4.242693700
6      -0.005528300    -0.882294000    -4.756160600
1      -0.005515000    -1.397431100    -5.554832100
6       1.258228400    -0.548790700    -4.243286900
7       1.470409200    -0.047753900    -3.028238100
7       1.473722100     0.076010900     3.021501300
```

6	1.266212200	0.552668100	4.242693900
6	0.005529700	0.882294100	4.756159500
1	0.005515000	1.397431100	5.554832100
6	-1.258227500	0.548790200	4.243287200
7	-1.470409200	0.047753900	3.028238100
6	-2.807147300	0.493994300	-2.791488800
1	-2.883670700	0.868519400	-1.761458900
1	-2.992699100	1.346894800	-3.465420700
1	-3.601774000	-0.254382800	-2.958077500
6	2.835994100	0.419045300	-2.772867600
1	3.371132200	0.629896400	-3.713205500
1	2.812876000	1.339204200	-2.170777300
1	3.414979600	-0.338158600	-2.215567700
1	2.128434700	-0.702705800	-4.898389600
1	-2.138491700	-0.708201700	-4.896342400
6	-2.835334100	-0.421125100	2.773458700
1	-3.370638100	-0.630180200	3.714114800
1	-3.415411200	0.333477500	2.213777900
1	-2.810704400	-1.343004100	2.174024400
1	-2.128464600	0.702628900	4.898372000
1	2.138425700	0.708061400	4.896461500
6	2.807455200	-0.493221300	2.791316300
1	2.882857700	-0.870438200	1.762185900
1	3.601470800	0.256552600	2.954527700
1	2.995077100	-1.343990400	3.467364300

*

Output files from all the calculations can be obtained by one of us (MA) on request.

Comparison of potential energy surfaces resulting from scalar relativistic (spin-free, no SOC, S=3/2, two roots) and spin-orbit coupling (SOC, S=3/2, 40 roots) calculation, exemplified using the vibronic distortions along the *q* effective symmetry breaking normal mode (see Figure 4a).

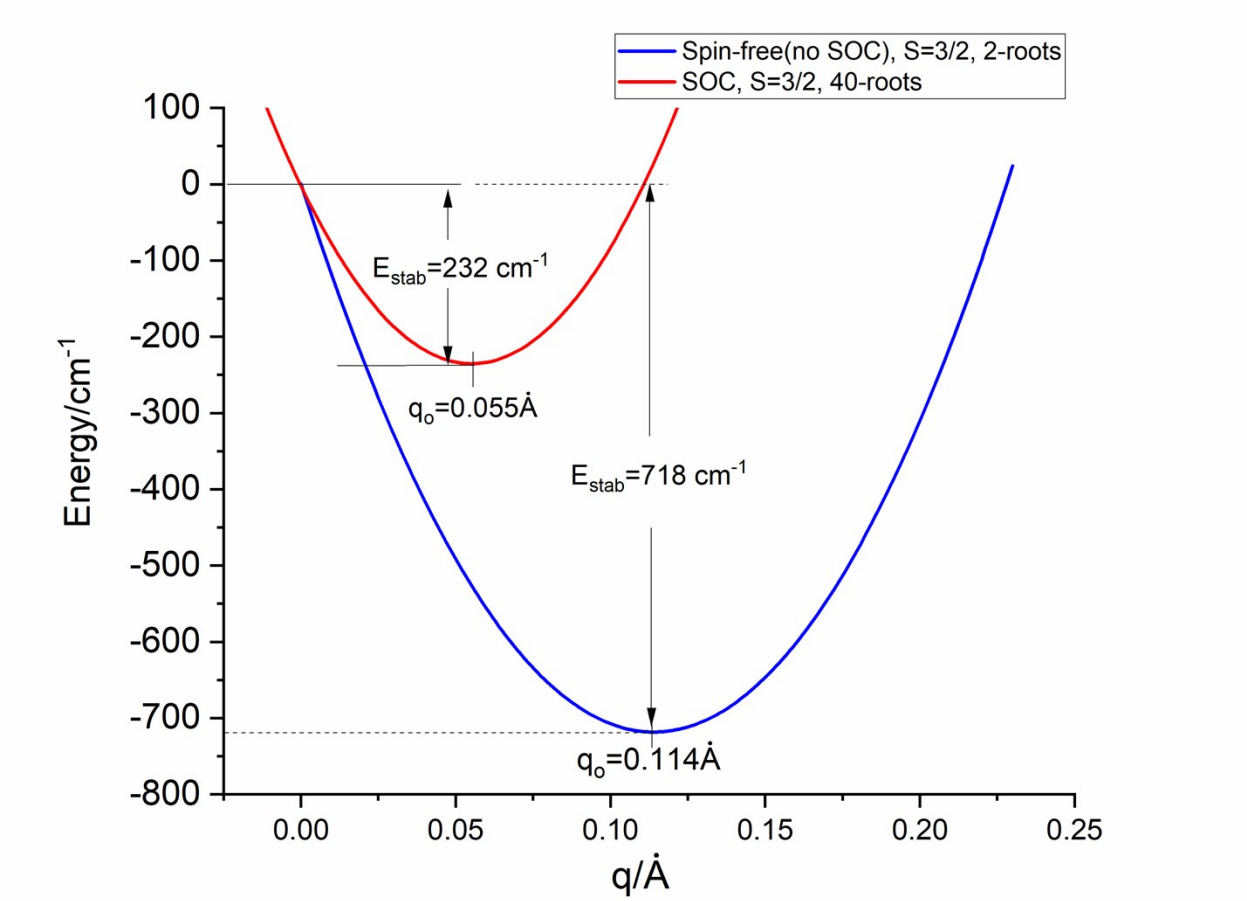

Figure S1. Ground state energy stabilizations E_{stab} and geometrical distortions as quantified by the shift along the q –symmetry breaking effective normal mode from CASSCF/NEVPT2 state specific scalar relativistic calculations using the two lowest S=3/2 spin states (roots, blue trace), and the spin-orbit coupling calculations of the lowest Kramer's quartet (S=3/2 state) resulting from diagonalization of the spin-orbit coupling Hamiltonian within the scalar relativistic many-particle basis of the lowest 40 scalar relativistic states (roots, red trace). Compared to the scalar relativistic result accounting for spin-orbit coupling reduces the stabilization energy E_{stab} by a factor of three and the vibronic distortion quantified by the shift along the effective symmetry breaking mode (q_o) by a factor of 2; reference geometry corresponding to q=0 is the one given by the X-ray structure of the $N_2Fe^{+2.5}\mu Te_2Fe^{+2.5}N_2$ core.