

Supplementary Materials for

Metal-Metal Bonding in Actinide Dimers: U₂ and U₂⁻

Sandra M. Ciborowski¹, Abhishek Mitra², Rachel M. Harris¹, Gaoxiang Liu¹, Prachi Sharma³, Navneet Khetrapal³, Moritz Blankenhorn¹, Laura Gagliardi^{2*}, and Kit H. Bowen^{1*}

Correspondence to: kbowen@jhu.edu (K.H.B.) and lgagliardi@uchicago.edu (L.G.)

This PDF file includes:

Supplementary Text

Figs. S1 to S3

Tables S1 to S6

Sample Input Files S1 to S3

Supplementary Text

The lowest lying electronic states for U_2^- using state-averaged CASSCF averaged over the three lowest states are presented in Fig. S2. It is interesting to note that the MS-CASPT2 corrections change the ordering of the lowest lying electronic states obtained from SA-CASSCF. According to SA-CASSCF, 8Q_u is the electronic ground state, however MS-CASPT2 corrections identify the ground state as 8O_u . The inclusion of dynamical correlation effects using MS-CASPT2 corrections play an important role in describing the equilibrium bond length, since it shifts the equilibrium bond length along with changing the ground state symmetry.

For all the electronic structure calculations, the anti-bonding $7s\sigma_u$ has been added to the active space orbitals used by Gagliardi et. al¹. Therefore, the new active spaces used are (6, 21) and (7, 21) for U_2 and U_2^- respectively where (n, m) indicates that n electrons can freely occupy m orbitals. The electron occupancies in Fig. 5 suggest the importance of including the extra orbital in explaining U_2^- bonding (Fig. 5). As reported in the original work on U_2 by Gagliardi et. al.¹, the $7s\sigma_g$ and $6d\pi_u$ orbitals form a strong triple bond and could therefore be left out of the active space.

Figure S3 presents the ground electronic state for U_2^- after spin-orbit coupling effects were taken into account. The points very close to the equilibrium geometry have also been quadratically fitted to get the precise bond length of 2.4329 Å. Due to spin-orbit coupling effects the total angular momentum Ω for the ground state becomes 7.5 a. u. and the ground state can be expressed as by the term symbol 7.5_u (Hund's case (c)). A state with $\Omega=8.5$ lies a mere 91 cm⁻¹ above the $\Omega=7.5$. It should be noted similarly that the ground state with $\Omega=9$ observed for U_2 by Knecht et. al², lies 280 cm⁻¹ higher than the $\Omega=8$ at 2.42 Angstroms.

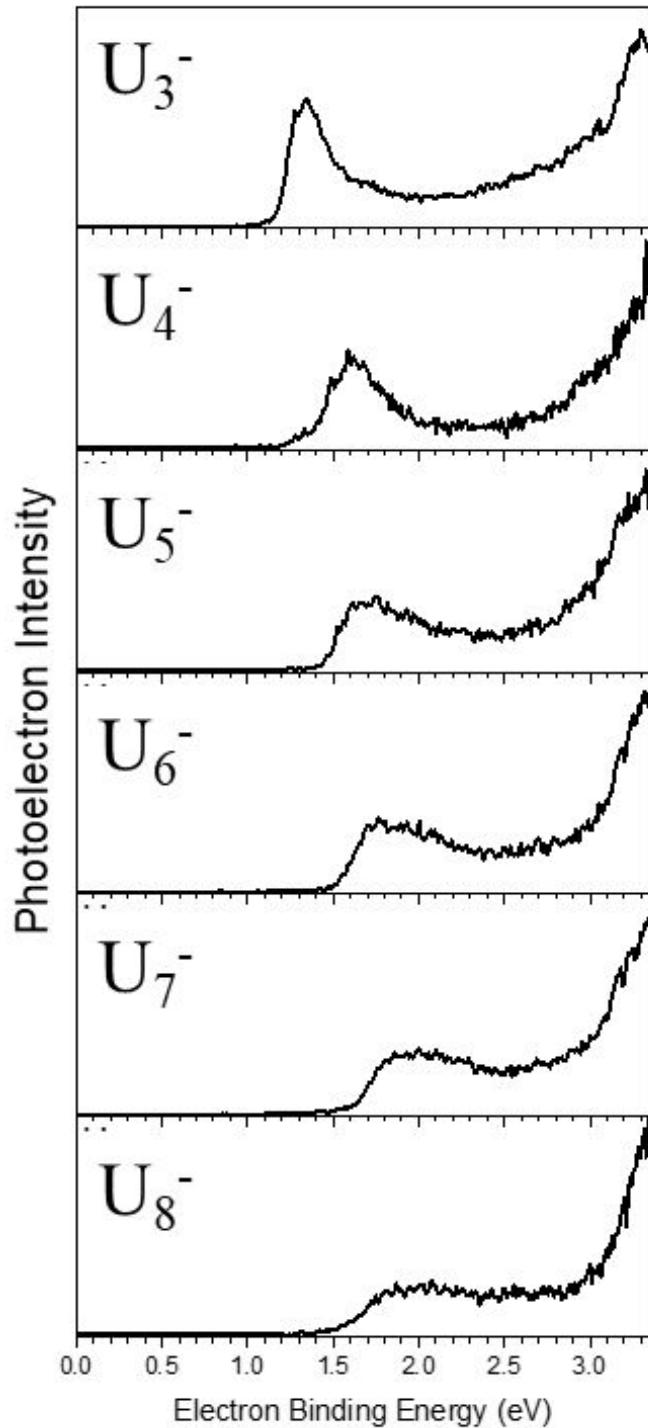


Fig. S1.

Anion Photoelectron Spectra of the Uranium Cluster Anions, U_n^- ($n = 3 - 8$).

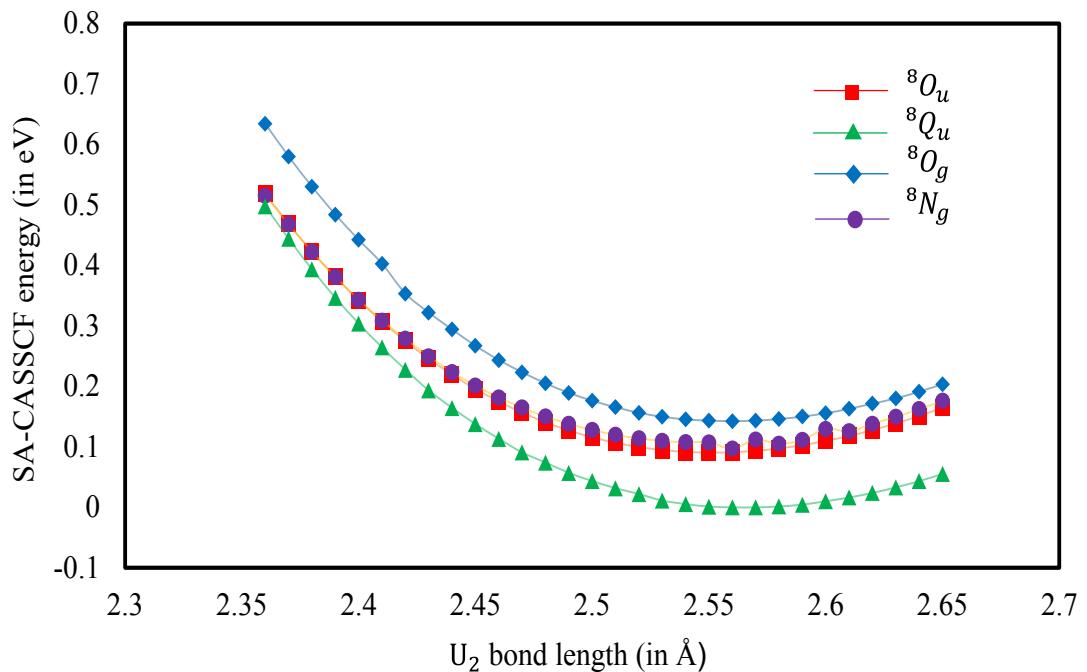


Fig. S2.

State-averaged CASSCF potential energy curves for the lowest lying electronic states of U_2^- around the equilibrium geometry.

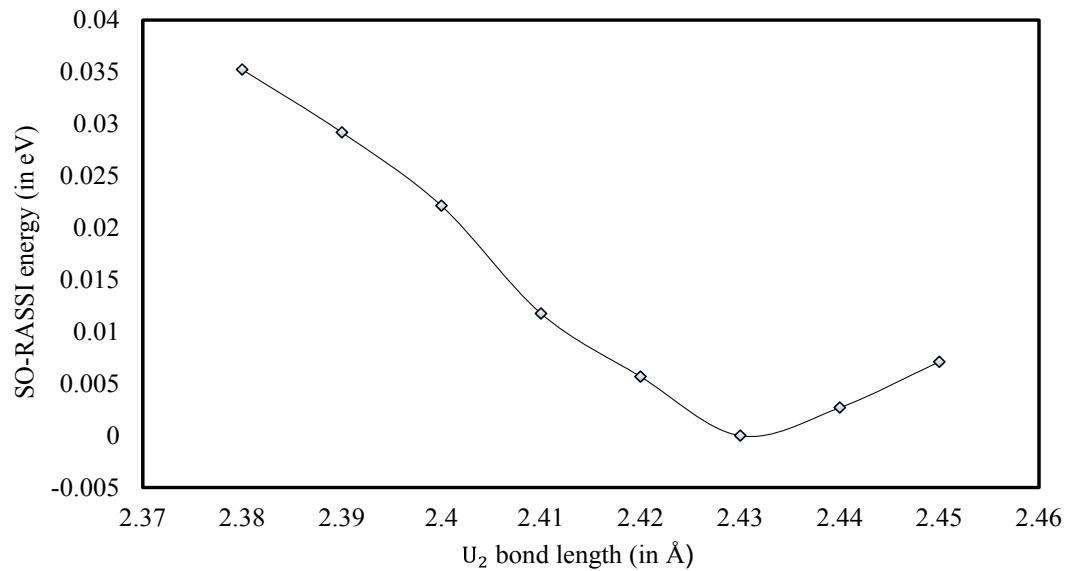


Fig. S3.

Ground state electronic energies (7.5u) for U₂⁻ around the equilibrium geometry using the MS-CASPT2 level of theory after inclusion of spin-orbit coupling effects.

Table S1.

Comparing minimum energies for uranium dimer and uranium dimer anion – MS-CASPT2.

	$E(U_2)$ CAS[6,21]	$E(U_2)$ CAS[7,21]	Difference ($E(U_2)$ – $E(U_2)$) (eV)
MS-CASPT2	-55900.32950	-55900.34993	0.56
State Average -3			
MS-CASPT2	-55900.32729	-55900.34917	0.60
State Average -10			
MS-CASPT2	-55900.32316	-55900.34825	0.68
State Average -20			
MS-CASPT2	-55900.32254	-55900.34826	0.70
State Average -30			

Table S2.

Absolute SO-RASSI energies for the naked uranium dimer and uranium dimer anions near their equilibrium geometries. The minimum geometries have been highlighted and used to calculate the electron affinity. An equilibrium bond length of 2.4329 Å is interpolated through fitting the points to a quadratic polynomial.

Bond length (Å)	Absolute energies of U_2 (au)	Absolute energies of U_2^- (au)	Electron Affinity (eV)
2.45		-55900.3991	
2.44		-55900.39926	
2.43	-55900.37306	-55900.39936	
2.42	-55900.37327	-55900.39915	0.71
2.41	-55900.37316	-55900.39893	
2.4	-55900.37307	-55900.39855	

Table S3.

MS-CASPT2 energies (in eV) for U_2^- relative to the ground state equilibrium geometry for the 8O_u , 8N_g , 8O_g and 8Q_u states. Data plotted in Fig. 4.

Bond length (\AA)	8O_u	8N_g	8O_g	8Q_u
2.35	0.06	0.21	0.16	0.16
2.36	0.05	0.18	0.14	0.14
2.37	0.03	0.17	0.12	0.11
2.38	0.02	0.16	0.10	0.10
2.39	0.02	0.15	0.10	0.09
2.4	0.01	0.14	0.09	0.08
2.41	0.01	0.14	0.08	0.07
2.42	0.00	0.15	0.06	0.07
2.43	0.00	0.15	0.05	0.07
2.44	0.00	0.15	0.06	0.07
2.45	0.01	0.16	0.06	0.07
2.46	0.01	0.17	0.07	0.08
2.47	0.02	0.18	0.08	0.08
2.48	0.03	0.20	0.08	0.10
2.49	0.04	0.21	0.09	0.10
2.5	0.06	0.23	0.11	0.12
2.51	0.07	0.25	0.12	0.13
2.52	0.08	0.27	0.13	0.14
2.53	0.10	0.29	0.15	0.15
2.54	0.12	0.31	0.17	0.17
2.55	0.14	0.34	0.19	0.19

Table S4.

State-averaged CASSCF energies (in eV) for U₂⁻ relative to the ground state equilibrium geometry for the ⁸O_u, ⁸N_g, ⁸O_g and ⁸Q_u states. Data plotted in Fig. S2.

Bond length (Å)	⁸ O _u	⁸ N _g	⁸ O _g	⁸ Q _u
2.36	0.52	0.52	0.63	0.50
2.37	0.47	0.47	0.58	0.44
2.38	0.42	0.42	0.53	0.39
2.39	0.38	0.38	0.48	0.35
2.4	0.34	0.34	0.44	0.30
2.41	0.31	0.31	0.40	0.26
2.42	0.28	0.28	0.35	0.23
2.43	0.25	0.25	0.32	0.19
2.44	0.22	0.22	0.29	0.16
2.45	0.20	0.20	0.27	0.14
2.46	0.18	0.18	0.24	0.11
2.47	0.16	0.17	0.22	0.09
2.48	0.14	0.15	0.21	0.07
2.49	0.13	0.14	0.19	0.06
2.5	0.12	0.13	0.18	0.04
2.51	0.11	0.12	0.17	0.03
2.52	0.10	0.11	0.16	0.02
2.53	0.09	0.11	0.15	0.01
2.54	0.09	0.11	0.15	0.01
2.55	0.09	0.11	0.14	0.00
2.56	0.09	0.10	0.14	0.00
2.57	0.09	0.11	0.14	0.00
2.58	0.10	0.11	0.15	0.00
2.59	0.10	0.11	0.15	0.00
2.6	0.11	0.13	0.16	0.01
2.61	0.12	0.13	0.16	0.02
2.62	0.13	0.14	0.17	0.02
2.63	0.14	0.15	0.18	0.03
2.64	0.15	0.16	0.19	0.04
2.65	0.16	0.18	0.20	0.06

Table S5.
SO-RASSI energies (in eV) relative to the equilibrium geometry for the ground state of U_2^- . Data plotted in Fig. S3.

Bond length (\AA)	$7.5u$
2.38	0.035
2.39	0.029
2.4	0.022
2.41	0.012
2.42	0.006
2.43	0.000
2.44	0.003
2.45	0.007

Table S6.

Calculated properties of U_2 and U_2^- . In the following results, the energy of U is -27950.17762 *au* and the energy of U^- is -27950.18128 *au* after spin orbit corrections are added.

Property	U_2 (CASPT2)	U_2 (CASPT2-SO)	U_2^- (CASPT2)	U_2^- (CASPT2-SO)
Total energy, $R = R_e$	-55900.32250	-55900.37327	-55900.34803	-55900.39936
Total energy, $R = R_{\square}$	-55900.26651	-55900.35524	-55900.26371	-55900.35890
D_e (eV)	1.52	0.48	2.29	1.09
R_e (A°)		2.42		2.43
w_e (cm-1)		265.32		220.41

Samples Input Files

Sample Input S1.

Sample input file for state-averaged CASSCF and MS-CASPT2 calculations on U_2^- . The particular example under consideration here calculates the CASSCF and MS-CASPT2 energies averaged over the first three states for 8O_u symmetry specie. The file labelled u2.xyz here contains the geometry for the system under consideration. The methods are described in further details in the “Materials and Methods” section.

```
>>> Export MOLCAS_MOLDEN=ON

&gateway
coord = u2.xyz
Basis set = U.ano-rcc.Roos.26s23p17d13f5g3h.9s8p6d4f2g.
Group = X Y Z
RICD
End

&SEWARD

>> COPY /$CurrDir/inp.RasOrb INPORB

&RASSCF &END
LUMORB
Linear
Symmetry = 3
nactel = 7 0 0
inactive = 20 11 11 4 19 10 10 4
ras2 = 4 2 2 2 5 2 2 2
spin = 8
ciroot = 3 3 1
ORBLISTING
ALL
End of Input

>> COPY $Project.RasOrb $CurrDir/$Project.Q.RasOrb
>> COPY $Project.JobIph $CurrDir/$Project.Q.JobIph

&CASPT2 &END
Noprop
Imaginary Shift
0.2
IPEA
0.25
Multistate
3 1 2 3
```

```
>> COPY $Project.JobMix $CurrDir/$Project.Q.JobMix
```

```
&GRID_IT
```

```
Sparse
```

```
all
```

```
end
```

Sample Input S2:

The sample input file for the a posteriori spin-orbit couple calculations in MOLCAS is presented. In the example shown, MS-CASPT2 calculations are performed on CASSCF wave-functions averaged over the first ten states. The Jobmix files from each spin and symmetry states are used in the RASSI module to compute the spin-orbit coupling energies. In the example below, there are 20 Jobmix files.

```
>>> Export MOLCAS_MOLDEN=ON

&gateway
coord = u2.xyz
Basis set = U.ano-rcc.Roos.26s23p17d13f5g3h.9s8p6d4f2g.
Group = X Y Z
RICD
Angmom
0.0 0.0 0.0
End

&SEWARD

>> COPY $CurrDir/inp.RasOrb INPORB
>> COPY $CurrDir/“Jobmix 1 file name” JOB001 >> COPY $CurrDir/“Jobmix 2 file name”
JOB002 . . . >> COPY $CurrDir/“Jobmix 20 file name” JOB020
&RASSI
eJOB
NR OF JOBIPHS= 20 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10
1 2 3 4 5 6 7 8 9 10; 1 2 3 4 5 6 7 8 9 10; 1 2 3 4 5 6 7 8 9 10; 1 2 3 4 5 6 7 8 9 10; 1 2 3
4 5 6 7 8 9 10; 1 2 3 4 5 6 7 8 9 10; 1 2 3 4 5 6 7 8 9 10; 1 2 3 4 5 6 7 8 9; 1 2 3 4 5 6 7 8
9 10; 1 2 3 4 5 6 7 8 9 10; 1 2 3 4 5 6 7 8 9 10; 1 2 3 4 5 6 7 8 9 10; 1 2 3 4 5 6 7 8 9 10;
1 2 3 4 5 6 7 8 9 10; 1 2 3 4 5 6 7 8 9 10; 1 2 3 4 5 6 7 8 9 10; 1 2 3 4 5 6 7 8 9 10; 1 2
3 4 5 6 7 8 9 10; 1 2 3 4 5 6 7 8 9 10; 1 2 3 4 5 6 7 8 9 10;
SPINorbit
end
```

Sample Input S3: The sample input file is an example for calculating a vibrational-rotational spectrum for U₂⁻ using the VIBROT program in OpenMolcas. The input parameters include the absolute energies (a.u.) and bond distances (in a.u.).

```
VIBROT
RoVibrational spectrum
Title = Vib-Rot spectrum for UU CAS(7,21)
Atoms = 0 U 0 U
Potential
4.497547853 -55900.398063530
4.516445113 -55900.398285690
4.535342373 -55900.398545200
4.554239633 -55900.398926130
4.573136892 -55900.399149660
4.592034152 -55900.399358520
4.610931412 -55900.399259450
4.629828672 -55900.399097100
Plot = 1.0 8.5 0.05
Grid = 150
Range = 1.0 10.0
Vibrations = 10
Rotations = 2 10
Orbital = 2
```

Sample Input S4: Sample input file for state-averaged CASSCF and MS-CASPT2 calculations on U⁻. The particular example under consideration here calculates the CASSCF and MS-CASPT2 energies averaged over the first thirty-eight states for symmetry species in the D₂ Irrep. The file labelled u.xyz here contains an U atom. The keyword CHARge can be used to differentiate between a neutral and charged specie. The methods are described in further details in the “Materials and Methods” section.

```
>>> Export MOLCAS_MOLDEN=ON

&gateway
coord = u.xyz
Basis set = U.ano-rcc.Roos.26s23p17d13f5g3h.9s8p6d4f2g.
Group = XY XZ
RICD
End

&SEWARD

&RASSCF &END
LUMORB
ATOM
Symmetry = 3
NACTEL = 7 0 0
inactive = 13 10 10 10
ras2 = 4 4 4 4
CHARge = -1
spin = 6
ciroot = 38 38 1
ORBLISTING
ALL
End of Input

>> COPY $Project.RasOrb $CurrDir/$Project.Q.RasOrb
>> COPY $Project.JobIph $CurrDir/$Project.Q.JobIph

&CASPT2 &END
Noprop
Imaginary Shift
0.2
IPEA
0.25
Multistate
38 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34
35 36 37 38

>> COPY $Project.JobMix $CurrDir/$Project.Q.JobMix
```

```
&GRID_IT
Sparse
all
end
```

Sample Input S5: Similar to Sample Input S2, the file here accounts for the a posteriori spin-orbit couple calculations in MOLCAS for the U⁻ atom. In the example shown, MS-CASPT2 calculations are performed on CASSCF wave-functions averaged over the first thirty-eight states. The Jobmix files from each spin and symmetry states are used in the RASSI module to compute the spin-orbit coupling energies. In the example below, there are 12 Jobmix files.

```
>>> Export MOLCAS_MOLDEN=ON
```

```
&gateway
coord = u.xyz
Basis set = U.ano-rcc.Roos.26s23p17d13f5g3h.9s8p6d4f2g.
Group = XY XZ
RICD
Angmom
0.0 0.0 0.0
End
```

&SEWARD

>> COPY \$CurrDir/inp.RasOrb INPORB

```
>> COPY $CurrDir/spin4sym1.JobMix JOB001
>> COPY $CurrDir/spin6sym1.JobMix JOB002
>> COPY $CurrDir/spin8sym1.JobMix JOB003
>> COPY $CurrDir/spin4sym2.JobMix JOB004
>> COPY $CurrDir/spin6sym2.JobMix JOB005
>> COPY $CurrDir/spin8sym2.JobMix JOB006
>> COPY $CurrDir/spin4sym3.JobMix JOB007
>> COPY $CurrDir/spin6sym3.JobMix JOB008
>> COPY $CurrDir/spin8sym3.JobMix JOB009
>> COPY $CurrDir/spin4sym4.JobMix JOB010
>> COPY $CurrDir/spin6sym4.JobMix JOB011
>> COPY $CurrDir/spin8sym4.JobMix JOB012
```

&RASSI
eJOB
J-VAalue
OMEGa
NR OF JOBIPHS= 12 38 38 38 38 38 38 38 38 38 38 38 38 38
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34
35 36 37 38; 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30
31 32 33 34 35 36 37 38; 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26
27 28 29 30 31 32 33 34 35 36 37 38; 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22
23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38; 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38; 1 2 3 4 5 6 7 8 9 10 11 12 13 14

```
15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38; 1 2 3 4 5 6 7 8 9 10  
11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38; 1 2 3 4  
5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37  
38; 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33  
34 35 36 37 38; 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29  
30 31 32 33 34 35 36 37 38; 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25  
26 27 28 29 30 31 32 33 34 35 36 37 38; 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21  
22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38;  
SPINorbit  
end
```