Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Ligand Field Theory, Pauli Shields and Ultra-covalency in Organometallic Chemistry

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Electronic Supporting Information

S0: Free ion Term energies as functions of interelectron repulsion parameters

Term symbol	Racah	Condon-Shortley
^{3}F	A – 8B	$F_0 – 8F_2 – 9F_4$
^{3}P	A + 7B	$F_0 + 7F_2 – 84F_4$
^{1}G	A + 4B + 2C	$F_0 + 4F_2 + F_4$
^{1}D	A – 3B + 2C	$F_0 – 3F_2 + 36F_4$
^{1}S	A + 14B + 7C	$F_0 + 14F_2 + 224F_4$

S1: aiLFT protocol

Using the DFT-optimised geometry – BP86 functional; Grimme dispersion corrections (keyword `D3BJ`); def2-SVP on all atoms except the metal where def2-TZVP is used; CPCM solvation field – the aiLFT protocol is as follows.

Step 1: We start with a single-point BP86 spin-restricted or unrestricted SCF calculation (same basis set and solvation field as used for the geometry optimisation) to generate a set of starting orbitals. If the system is paramagnetic, a quasi-restricted set of orbitals is requested (keyword `UNO`).

Step 2: The (restricted, quasi or otherwise) valence orbitals are analysed to establish whether they already provide a suitable starting active space. That is, are there 5 mainly-d orbitals spanning the HOMO/LUMO gap? This is usually the case for weak-field systems towards the ionic extreme and almost never the case for stronger field, more covalent systems. If necessary then, a series of single-SCF-step calculations (keyword `NoIter`) are undertaken where the required mostly-d orbitals are rotated to lie around the HOMO/LUMO gap as required.

Step 3: An (n,5) CASSCF/NEVPT2 calculation is run with the `actorbs` flag set to `dorbs` in order to invoke the aiLFT procedure. Normally, the number and spin degeneracies of the roots are chosen to match the Russell-Saunders terms arising from the d^n configuration.

S2: Cartesian coordinates in Å: S=0 unless otherwise stated

$[Fe(CO)_6]^{2+}$: O_h

Fe	0.000000000	-0.000002000	0.000000000
C	1.872078000	0.000004000	-0.000892000
C	0.000000000	1.875108000	0.000000000
C	-0.001966000	-0.000005000	1.873676000
C	-1.872079000	0.000004000	0.000892000
C	0.000000000	-1.875111000	0.000000000
C	0.001966000	-0.000005000	-1.873676000
O	3.006296000	0.000010000	-0.002564000
O	-0.000001000	3.009214000	0.000000000
O	-0.001889000	-0.000005000	3.007867000
O	-3.006297000	0.000011000	0.002563000
O	0.000000000	-3.009217000	0.000000000
O	0.001890000	-0.000004000	-3.007866000

$[Fe(CO)_6]^{2+}$: C_{3v}

Fe	0.000000000	-0.000002000	0.000000000
C	1.869858000	0.064926000	0.063982000
C	0.062018000	1.873053000	0.062107000
C	0.062142000	0.064205000	1.871545000
C	-1.869859000	-0.064924000	-0.063987000
C	-0.062018000	-1.873056000	-0.062107000
C	-0.062140000	-0.064212000	-1.871545000
O	3.002770000	0.104266000	0.101615000
O	0.099527000	3.005916000	0.099670000
O	0.101025000	0.103072000	3.004403000
O	-3.002771000	-0.104255000	-0.101625000
O	-0.099528000	-3.005919000	-0.099670000
O	-0.101020000	-0.103076000	-3.004402000

$[Mn(CO)_6]^{+}$: O_h

Mn	0.000000000	0.000000000	0.000000000
C	1.877708000	0.000000000	0.000000000
C	0.000000000	0.000000000	-1.877708000
C	0.000000000	1.877708000	0.000000000
C	-1.877708000	0.000000000	0.000000000
C	0.000000000	0.000000000	1.877708000
C	0.000000000	-1.877708000	0.000000000
O	3.022947000	0.000000000	0.000000000
O	0.000000000	0.000000000	-3.022947000
O	0.000000000	3.022947000	0.000000000
O	-3.022947000	0.000000000	0.000000000
O	0.000000000	0.000000000	3.022947000
O	0.000000000	-3.022947000	0.000000000

$[Mn(CO)_6]^+$: C_{3v}

Mn	0.000000000	0.000000000	0.000000000
C	-0.739827000	1.281418000	1.156032000
C	-1.479654000	0.000000000	-1.156032000
C	-0.739827000	-1.281418000	1.156032000
C	0.739827000	-1.281418000	-1.156032000
C	1.479654000	0.000000000	1.156032000
C	0.739827000	1.281418000	-1.156032000
O	-1.191057000	2.062972000	1.861112000
O	-2.382115000	0.000000000	-1.861112000
O	-1.191057000	-2.062972000	1.861112000
O	1.191057000	-2.062972000	-1.861112000
O	2.382115000	0.000000000	1.861112000
O	1.191057000	2.062972000	-1.861112000

$Cr(CO)_6$: O_h

Cr	0.000000000	0.000000000	0.000000000
C	1.900047000	0.000001000	0.000100000
C	0.000000000	1.900237000	0.000000000
C	-0.000107000	-0.000001000	1.900103000
C	-1.900048000	0.000001000	-0.000100000
C	-0.000001000	-1.900236000	0.000000000
C	0.000108000	0.000000000	-1.900103000
O	3.052922000	0.000001000	-0.000047000
O	-0.000001000	3.053083000	0.000000000
O	0.000087000	-0.000001000	3.052987000
O	-3.052922000	0.000001000	0.000046000
O	-0.000001000	-3.053083000	0.000001000
O	-0.000085000	0.000000000	-3.052987000

$Cr(CO)_6$ C_{3v}

Cr	0.000000000	0.000000000	0.000000000
C	1.497322000	0.000000000	1.169836000
C	-0.748661000	-1.296719000	1.169836000
C	0.748661000	-1.296719000	-1.169836000
C	-1.497322000	0.000000000	-1.169836000
C	0.748661000	1.296719000	-1.169836000
C	-0.748661000	1.296719000	1.169836000
O	2.405802000	0.000000000	1.879603000
O	-1.202901000	-2.083486000	1.879603000
O	1.202901000	-2.083486000	-1.879603000
O	-2.405802000	0.000000000	-1.879603000
O	1.202901000	2.083486000	-1.879603000
O	-1.202901000	2.083486000	1.879603000

$[V(CO)_6]^-$: O_h

V	0.000000000	0.000000000	0.000000000
C	-1.954093000	0.000000000	0.000000000
C	0.000000000	0.000000000	-1.954093000
C	0.000000000	-1.954093000	0.000000000
C	1.954093000	0.000000000	0.000000000
C	0.000000000	0.000000000	1.954093000

C	0.000000000	1.954093000	0.000000000
O	-3.127513000	0.000000000	0.000000000
O	0.000000000	0.000000000	-3.127513000
O	0.000000000	-3.127513000	0.000000000
O	3.127513000	0.000000000	0.000000000
O	0.000000000	0.000000000	3.127513000
O	0.000000000	3.127513000	0.000000000

$[V(CO)_6]^-$: C_{3v}

V	0.000000000	0.000000000	0.000000000
C	1.539846000	0.000000000	-1.203060000
C	-0.769923000	-1.333546000	-1.203060000
C	-0.769923000	1.333546000	-1.203060000
C	-1.539846000	0.000000000	1.203060000
C	0.769923000	1.333546000	1.203060000
C	0.769923000	-1.333546000	1.203060000
O	2.464514000	0.000000000	-1.925489000
O	-1.232257000	-2.134332000	-1.925489000
O	-1.232257000	2.134332000	-1.925489000
O	-2.464514000	0.000000000	1.925489000
O	1.232257000	2.134332000	1.925489000
O	1.232257000	-2.134332000	1.925489000

$[Ti(CO)_6]^{2-}$: O_h

Ti	0.000000000	0.000000000	0.000000000
C	0.000000000	0.000000000	2.042569000
C	0.000000000	2.042569000	0.000000000
C	-2.042569000	0.000000000	0.000000000
C	0.000000000	0.000000000	-2.042569000
C	0.000000000	-2.042569000	0.000000000
C	2.042569000	0.000000000	0.000000000
O	0.000000000	0.000000000	3.231090000
O	0.000000000	3.231090000	0.000000000
O	-3.231090000	0.000000000	0.000000000
O	0.000000000	0.000000000	-3.231090000
O	0.000000000	-3.231090000	0.000000000
O	3.231090000	0.000000000	0.000000000

$[Ti(CO)_6]^{2-}$: C_{3v}

Ti	0.000000000	0.000000000	0.000000000
C	-0.804783000	1.393925000	1.257531000
C	-0.804783000	-1.393925000	1.257531000
C	1.609566000	0.000000000	1.257531000
C	0.804783000	-1.393925000	-1.257531000
C	0.804783000	1.393925000	-1.257531000
C	-1.609566000	0.000000000	-1.257531000
O	-1.273067000	2.205016000	1.989258000
O	-1.273067000	-2.205016000	1.989258000
O	2.546134000	0.000000000	1.989258000
O	1.273067000	-2.205016000	-1.989258000
O	1.273067000	2.205016000	-1.989258000
O	-2.546134000	0.000000000	-1.989258000

$[Cu(CF_3)_4]^-$

Cu	-0.001427000	-0.001059000	0.000869000
C	-1.419680000	1.404616000	-0.206299000
C	1.404571000	1.417866000	0.202036000
C	-1.407666000	-1.419135000	0.205701000
C	1.417431000	-1.407398000	-0.197865000
F	-0.993614000	2.497884000	-0.921580000
F	-2.519229000	0.967669000	-0.904782000
F	-1.898189000	1.893943000	0.976383000
F	-2.503658000	-0.992590000	0.916468000
F	-1.892651000	-1.899975000	-0.977832000
F	-0.972403000	-2.517165000	0.907634000
F	0.992954000	-2.504611000	-0.907954000
F	1.895152000	-1.890378000	0.987753000
F	2.517304000	-0.973153000	-0.897562000
F	2.499243000	0.994136000	0.916531000
F	1.891702000	1.893417000	-0.982750000
F	0.968370000	2.519062000	0.898367000

$[Cu(CH_3)_4]^-$

Cu	0.000000000	0.000000000	0.000000000
C	1.410365000	1.410365000	-0.006697000
C	1.410365000	-1.410365000	0.006697000
C	-1.410365000	1.410365000	0.006697000
C	-1.410365000	-1.410365000	-0.006697000
H	-1.075921000	2.355434000	0.489879000
H	1.645179000	1.645179000	1.058005000
H	1.645179000	-1.645179000	-1.058005000
H	-1.075921000	-2.355434000	-0.489879000
H	-1.645179000	1.645179000	-1.058005000
H	-1.645179000	-1.645179000	1.058005000
H	2.355434000	-1.075921000	0.489879000
H	1.075921000	2.355434000	-0.489879000
H	-2.355434000	1.075921000	0.489879000
H	-2.355434000	-1.075921000	-0.489879000
H	1.075921000	-2.355434000	0.489879000
H	2.355434000	1.075921000	-0.489879000

$[Zn(CF_3)_4]^-$

Zn	-0.000111000	0.000212000	0.000088000
C	-1.193156000	-1.194210000	1.191616000
C	-1.191990000	1.194163000	-1.193196000
C	1.193144000	-1.194113000	-1.191287000
C	1.191926000	1.194352000	1.192966000
F	-2.065220000	-2.061476000	0.514488000
F	-0.514333000	-2.066385000	2.057930000
F	-2.060031000	-0.517467000	2.064783000
F	2.061014000	-0.517191000	-2.063300000
F	2.064206000	-2.062452000	-0.514247000
F	0.514410000	-2.065235000	-2.058757000
F	2.057826000	2.068239000	0.516346000

F	2.065012000	0.517243000	2.059607000
F	0.512942000	2.059720000	2.065900000
F	-2.064613000	0.517013000	-2.060262000
F	-2.058281000	2.067903000	-0.516895000
F	-0.512746000	2.059684000	-2.065781000

$[Ni(CF_3)_4]^{2-}$

Ni	-0.001427000	-0.001059000	0.000869000
C	-1.419680000	1.404616000	-0.206299000
C	1.404571000	1.417866000	0.202036000
C	-1.407666000	-1.419135000	0.205701000
C	1.417431000	-1.407398000	-0.197865000
F	-0.993614000	2.497884000	-0.921580000
F	-2.519229000	0.967669000	-0.904782000
F	-1.898189000	1.893943000	0.976383000
F	-2.503658000	-0.992590000	0.916468000
F	-1.892651000	-1.899975000	-0.977832000
F	-0.972403000	-2.517165000	0.907634000
F	0.992954000	-2.504611000	-0.907954000
F	1.895152000	-1.890378000	0.987753000
F	2.517304000	-0.973153000	-0.897562000
F	2.499243000	0.994136000	0.916531000
F	1.891702000	1.893417000	-0.982750000
F	0.968370000	2.519062000	0.898367000

$[Ni(CN)_4]^{2-}$

Ni	0.000000000	0.000000000	0.000000000
C	1.857673000	0.000001000	0.000091000
C	-1.857673000	-0.000001000	-0.000091000
C	0.000001000	1.857893000	0.000000000
C	-0.000001000	-1.857892000	0.000000000
N	3.040481000	0.000002000	-0.000055000
N	-3.040482000	-0.000001000	0.000055000
N	0.000002000	3.040720000	0.000000000
N	-0.000002000	-3.040720000	0.000000000

$[Cu(CN)_4]^{-}$

Cu	0.000000000	0.000000000	0.000000000
C	1.878960000	0.000000000	0.000000000
C	0.000000000	-1.878960000	0.000000000
C	-1.878960000	0.000000000	0.000000000
C	0.000000000	1.878960000	0.000000000
N	3.054937000	0.000000000	0.000000000
N	0.000000000	-3.054937000	0.000000000
N	-3.054937000	0.000000000	0.000000000
N	0.000000000	3.054937000	0.000000000

$[Cu(CF_3)_3(bipy)]$

Cu	0.268189000	-0.415974000	-0.178163000
C	1.792135000	-0.452148000	1.100831000
F	2.650451000	0.597100000	1.012883000
F	2.526533000	-1.595904000	0.982577000

F	1.345695000	-0.438685000	2.406011000
C	1.475916000	0.047007000	-1.650430000
F	2.755492000	-0.378216000	-1.500990000
F	1.519493000	1.416055000	-1.726886000
F	1.089439000	-0.403473000	-2.870727000
C	-1.281629000	-0.456313000	-1.425891000
F	-2.475481000	-0.429953000	-0.735206000
F	-1.312036000	-1.609262000	-2.155138000
F	-1.357924000	0.582097000	-2.297870000
C	-2.144554000	2.720134000	2.762726000
H	-2.706711000	3.372097000	3.447763000
C	-1.323833000	3.270132000	1.765718000
H	-1.221260000	4.357736000	1.643274000
C	-0.628002000	2.395300000	0.917461000
H	0.032617000	2.759000000	0.114627000
N	-0.727996000	1.064988000	1.036082000
C	-1.512575000	0.516752000	1.989434000
C	-2.243093000	1.327129000	2.879699000
H	-2.881279000	0.882547000	3.655054000
C	-2.249175000	-3.120545000	2.879123000
H	-2.835156000	-3.720903000	3.590678000
C	-2.294113000	-1.722038000	2.935658000
H	-2.913792000	-1.219337000	3.689663000
C	-1.538093000	-0.969734000	2.017685000
N	-0.774255000	-1.593788000	1.088001000
C	-0.723938000	-2.933572000	1.024912000
H	-0.079791000	-3.358833000	0.240622000
C	-1.450496000	-3.742914000	1.907299000
H	-1.387030000	-4.837144000	1.828748000

$Fe(Cp)_2$: D_{5h}

Fe	0.000000000	0.000000000	0.000000000
C	0.378824000	1.165902000	1.633775000
C	1.225902000	0.000000000	-1.633775000
C	1.225902000	0.000000000	1.633775000
C	-0.991775000	0.720567000	1.633775000
C	0.378824000	1.165902000	-1.633775000
C	0.378824000	-1.165902000	-1.633775000
C	0.378824000	-1.165902000	1.633775000
C	-0.991775000	-0.720567000	1.633775000
C	-0.991775000	0.720567000	-1.633775000
C	-0.991775000	-0.720567000	-1.633775000
H	0.717950000	2.209623000	1.612941000
H	2.323335000	0.000000000	-1.612941000
H	2.323335000	0.000000000	1.612941000
H	-1.879618000	1.365622000	1.612941000
H	0.717950000	2.209623000	-1.612941000
H	0.717950000	-2.209623000	-1.612941000
H	0.717950000	-2.209623000	1.612941000
H	-1.879618000	-1.365622000	1.612941000
H	-1.879618000	1.365622000	-1.612941000
H	-1.879618000	-1.365622000	-1.612941000

$Cr(C_6H_6)_2$: D_{6h}

Cr	0.000000000	0.000000000	0.000000000
C	1.427753000	0.000000000	1.589558000
H	2.527962000	0.000000000	1.529310000
C	0.713896000	1.236425000	1.588541000
H	1.264462000	2.188639000	1.526832000
C	-0.713896000	1.236425000	1.588541000
H	-1.264462000	2.188639000	1.526832000
C	-1.427753000	0.000000000	1.589558000
H	-2.527962000	0.000000000	1.529310000
C	-0.713896000	-1.236425000	1.588541000
H	-1.264462000	-2.188639000	1.526832000
C	0.713896000	-1.236425000	1.588541000
H	1.264462000	-2.188639000	1.526832000
C	1.427753000	0.000000000	-1.589559000
H	2.527962000	0.000000000	-1.529310000
C	0.713896000	1.236425000	-1.588541000
H	1.264462000	2.188639000	-1.526832000
C	-0.713896000	1.236425000	-1.588541000
H	-1.264462000	2.188639000	-1.526832000
C	-1.427753000	0.000000000	-1.589559000
H	-2.527962000	0.000000000	-1.529310000
C	-0.713896000	-1.236425000	-1.588542000
H	-1.264462000	-2.188639000	-1.526832000
C	0.713896000	-1.236425000	-1.588541000
H	1.264462000	-2.188639000	-1.526832000

$V(Cp)_2$: D_{5d} S=3/2

V	0.000000000	0.000000000	0.000000000
C	1.160191000	-0.376969000	1.907557000
C	0.717037000	-0.986917000	-1.907557000
C	0.000000000	-1.219897000	1.907557000
C	0.717037000	0.986917000	1.907557000
C	1.160191000	0.376969000	-1.907557000
C	-0.717037000	-0.986917000	-1.907557000
C	-1.160191000	-0.376969000	1.907557000
C	-0.717037000	0.986917000	1.907557000
C	0.000000000	1.219897000	-1.907557000
C	-1.160191000	0.376969000	-1.907557000
H	2.204286000	-0.716216000	1.902708000
H	1.362323000	-1.875077000	-1.902708000
H	0.000000000	-2.317723000	1.902708000
H	1.362323000	1.875077000	1.902708000
H	2.204286000	0.716216000	-1.902708000
H	-1.362323000	-1.875077000	-1.902708000
H	-2.204286000	-0.716216000	1.902708000
H	-1.362323000	1.875077000	1.902708000
H	0.000000000	2.317723000	-1.902708000
H	-2.204286000	0.716216000	-1.902708000

$Ni(Cp)_2$: D_{5h} S=1

Ni	0.000000000	0.000000000	0.000000000
C	-0.377152000	-1.160754000	-1.829592000
H	-0.716297000	-2.204535000	-1.825892000
C	-1.220489000	0.000000000	-1.829592000
H	-2.317985000	0.000000000	-1.825892000
C	-0.377152000	1.160754000	-1.829592000
H	-0.716297000	2.204535000	-1.825892000
C	0.987396000	0.717385000	-1.829592000
H	1.875289000	1.362477000	-1.825892000
C	0.987396000	-0.717385000	-1.829592000
H	1.875289000	-1.362477000	-1.825892000
C	-0.377152000	-1.160754000	1.829592000
H	-0.716297000	-2.204535000	1.825892000
C	-1.220489000	0.000000000	1.829592000
H	-2.317985000	0.000000000	1.825892000
C	-0.377152000	1.160754000	1.829592000
H	-0.716297000	2.204535000	1.825892000
C	0.987396000	0.717385000	1.829592000
H	1.875289000	1.362477000	1.825892000
C	0.987396000	-0.717385000	1.829592000
H	1.875289000	-1.362477000	1.825892000

$[Ni(Cp)_2]^{2+}$: D_{5d}

Ni	0.000000000	0.000000000	0.000000000
C	1.166448000	-0.379002000	1.656697000
C	0.720904000	-0.992240000	-1.656697000
C	0.000000000	-1.226476000	1.656697000
C	0.720904000	0.992240000	1.656697000
C	1.166448000	0.379002000	-1.656697000
C	-0.720904000	-0.992240000	-1.656697000
C	-1.166448000	-0.379002000	1.656697000
C	-0.720904000	0.992240000	1.656697000
C	0.000000000	1.226476000	-1.656697000
C	-1.166448000	0.379002000	-1.656697000
H	2.209428000	-0.717887000	1.611874000
H	1.365502000	-1.879452000	-1.611874000
H	0.000000000	-2.323130000	1.611874000
H	1.365502000	1.879452000	1.611874000
H	2.209428000	0.717887000	-1.611874000
H	-1.365502000	-1.879452000	-1.611874000
H	-2.209428000	-0.717887000	1.611874000
H	-1.365502000	1.879452000	1.611874000
H	0.000000000	2.323130000	-1.611874000
H	-2.209428000	0.717887000	-1.611874000

$[NiF_6]^{2-}$: O_h

Ni	0.000000000	0.000000000	0.000000000
F	-1.809821000	0.000000000	0.000000000
F	0.000000000	0.000000000	1.809821000
F	0.000000000	1.809821000	0.000000000
F	1.809821000	0.000000000	0.000000000
F	0.000000000	0.000000000	-1.809821000

F	0.000000000	-1.809821000	0.000000000

$[Fe(CN)_6]^{3-}$: D_{4h} S=1/2

Fe	0.000000000	0.000000000	0.000000000
C	0.000000000	0.000000000	1.918398000
C	0.000000000	1.926837000	0.000000000
C	-1.926837000	0.000000000	0.000000000
C	0.000000000	0.000000000	-1.918398000
C	0.000000000	-1.926837000	0.000000000
C	1.926837000	0.000000000	0.000000000
N	0.000000000	0.000000000	3.094168000
N	0.000000000	3.101754000	0.000000000
N	-3.101754000	0.000000000	0.000000000
N	0.000000000	0.000000000	-3.094168000
N	0.000000000	-3.101754000	0.000000000
N	3.101754000	0.000000000	0.000000000

$[Fe(CN)_6]^{-}$: O_h S=3/2

Fe	0.000000000	0.000000000	0.000000000
C	1.921513664	0.000000000	0.000000000
C	0.000000000	0.000000000	1.921513672
C	0.000000000	-1.921513664	0.000000000
C	-1.921513664	0.000000000	0.000000000
C	0.000000000	0.000000000	-1.921513672
C	0.000000000	1.921513664	0.000000000
N	3.095541831	0.000000000	0.000000000
N	0.000000000	0.000000000	3.095541838
N	0.000000000	-3.095541831	0.000000000
N	-3.095541831	0.000000000	0.000000000
N	0.000000000	0.000000000	-3.095541838
N	0.000000000	3.095541831	0.000000000

$[CrF_6]^{-}$: D_{4h} S=1/2

Cr	0.000000000	0.000000000	0.000000000
F	0.000000000	0.000000000	1.765137000
F	0.000000000	1.792472000	0.000000000
F	-1.792472000	0.000000000	0.000000000
F	0.000000000	0.000000000	-1.765137000
F	0.000000000	-1.792472000	0.000000000
F	1.792472000	0.000000000	0.000000000

S3: Selected aiLFT and CLF analyses of selected ML_4 systems

DFT-optimised geometries (ESI S2) employed throughout.

$[Cu(CF_3)_4]^-$

aiLFT CAS active space orbital energies: NB X and Y axes bisect C-Cu-C angles

Orbital	Energy (eV)	Energy(cm-1)	dxy	dyz	dz2	dxz	dx2-y2
1	0.000	0.0	0.001788	-0.958033	0.004196	0.286616	0.001618
2	0.000	2.1	0.002130	0.286624	0.000857	0.958039	-0.001370
3	0.139	1120.7	0.000020	0.003777	0.999990	-0.002022	0.001164
4	0.246	1984.7	0.012653	0.001953	-0.001169	0.000819	0.999917
5	4.788	38617.3	-0.999916	-0.001078	0.000014	0.002564	0.012653

AOM/CLF d-orbital energies (cm-1): $e_\sigma(CF_3)$ = 12500; e_σ(void) = -7000; e_π(void) -1400 (NB Cu-C bonds aligned along X and Y axes.)

E	dz2	dyz	dxz	dxy	dx2-y2
36695	-0.0000	0.0000	0.0000	-0.0000	1.0000
0	0.0000	-0.0000	-0.0000	1.0000	0.0000
-793	0.9992	0.0000	0.0000	-0.0000	0.0000
-1979	-0.0000	-0.2341	0.9722	-0.0000	0.0000
-1979	0.0000	-0.9722	-0.2341	-0.0000	0.0000

aiLFT NEVPT2 active space orbital energies: NB X and Y axes bisect C-Cu-C angles

Orbital	Energy (eV)	Energy(cm-1)	dxy	dyz	dz2	dxz	dx2-y2
1	0.000	0.0	0.012652	0.001932	0.000837	0.000595	0.999918
2	0.128	1032.3	0.001769	-0.960306	0.004478	0.278901	0.001663
3	0.129	1036.9	0.002164	0.278909	0.000893	0.960314	-0.001138
4	0.194	1563.9	0.000012	-0.004050	-0.999989	0.002107	0.000844
5	8.170	65897.8	-0.999916	-0.001070	0.000008	0.002579	0.012653

AOM/CLF d-orbital energies (cm-1): $e_\sigma(CF_3)$ = 22450; e_σ(void) = -9900; e_π(void) -200 (NB X and Y axes bisect C-Cu-C angles.)

E	dz2	dyz	dxz	dxy	dx2-y2
65892	-0.0000	0.0000	-0.0000	1.0000	0.0000
1605	-1.0000	0.0000	0.0000	-0.0000	0.0000
1062	0.0000	0.3650	0.9310	-0.0000	-0.0000
1062	-0.0000	0.9310	-0.3650	-0.0000	0.0000
0	-0.0000	-0.0000	-0.0000	0.0000	-1.0000

$[Cu(CH_3)_4]^-$

aiLFT CAS active space orbital energies: NB X and Y axes bisect C-Cu-C angles

Orbital	Energy (eV)	Energy(cm-1)	dxy	dyz	dz2	dxz	dx2-y2
1	0.000	0.0	0.000004	0.999960	-0.000001	-0.008949	-0.000000
2	0.000	0.0	0.000000	0.008949	0.000469	0.999960	-0.000002
3	0.026	211.3	-0.000000	0.000003	-1.000000	0.000469	0.000007
4	0.490	3953.9	0.000000	0.000000	0.000007	0.000002	1.000000
5	5.062	40829.6	1.000000	-0.000004	-0.000000	-0.000000	-0.000000

aiLFT NEVPT2 active space orbital energies: NB X and Y axes bisect C-Cu-C angles

Orbital	Energy (eV)	Energy(cm-1)	dxy	dyz	dz2	dxz	dx2-y2
1	0.000	0.0	0.000000	0.018795	0.000202	-0.999823	0.000040
2	0.000	0.0	-0.000005	-0.999823	0.000005	-0.018795	0.000001
3	0.184	1480.8	0.000000	0.000001	1.000000	0.000202	-0.000027
4	0.376	3033.2	0.000000	-0.000000	0.000027	0.000040	1.000000
5	8.930	72024.1	-1.000000	0.000005	0.000000	0.000000	0.000000

$[Ni(CF_3)_4]^{2-}$

Orbital	Energy (eV)	Energy(cm-1)	dxy	dyz	dz2	dxz	dx2-y2
1	0.000	0.0	-0.001628	0.928348	-0.003599	-0.371686	-0.001684

2	0.000	0.5	0.001712	0.371689	-0.000074	0.928355	-0.001601
3	0.038	309.6	-0.000012	0.003370	0.999993	-0.001269	0.000300
4	0.280	2255.0	0.010205	0.002166	-0.000306	0.000839	0.999945
5	2.955	23833.5	-0.999945	-0.000853	-0.000010	0.002203	0.010205

$[Ni(CN)_4]^{2-}$

Orbital	Energy (eV)	Energy(cm-1)	dxy	dyz	dz2	dxz	dx2-y2
1	0.000	0.0	-0.000261	0.999975	-0.000005	0.007012	-0.000001
2	0.000	0.3	-0.000002	0.007012	0.000659	-0.999975	0.000077
3	0.085	682.3	-0.000000	0.000000	-1.000000	-0.000659	-0.000027
4	0.208	1681.1	-1.000000	-0.000261	0.000000	-0.000000	0.000000
5	3.544	28585.4	0.000000	0.000000	-0.000027	0.000077	1.000000

AOM/CLF d-orbital energies relative to d_{xz}/d_{yz} at zero. (cm-1): $e_\sigma(CN)$ = 8400; $e_\pi(CN)$ = -400 $e_\sigma(void)$ = -5850; $e_\pi(void)$ = -1200 (NB Cu-C bonds aligned along X and Y axes. * fixed assumed value)*

E	dz2	dyz	dxz	dxy	dx2-y2
28400	0.0000	0.0000	0.0000	0.0000	1.0000
1600	-0.0000	0.0000	-0.0000	1.0000	0.0000
733	-0.9996	0.0000	-0.0000	-0.0000	0.0000
0	0.0000	-0.0000	-1.0000	-0.0000	0.0000
0	0.0000	1.0000	-0.0000	-0.0000	0.0000

$[Cu(CN)_4]^{-}$

Orbital	Energy (eV)	Energy(cm-1)	dxy	dyz	dz2	dxz	dx2-y2
1	0.000	0.0	0.000001	1.000000	-0.000000	0.000000	-0.000000
2	0.000	1.5	0.000000	0.000000	0.000187	-1.000000	0.000007
3	0.073	589.6	0.000000	-0.000000	-1.000000	-0.000187	-0.000003
4	0.415	3343.4	1.000000	-0.000001	0.000000	0.000000	0.000000
5	5.006	40376.6	-0.000000	0.000000	-0.000003	0.000007	1.000000