Supporting Information for:

Density functional theory and DFT+U study of transition metal porphine adsorbed on Au(111) surfaces and effects of applied electric fields

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1: DFT+U implementation

Following Bengone *et al.*,[1] we describe the projected augmented wave (PAW)[2]-based, DFT+U implementation used in VASP version 4.6.

The DFT+U total energy functional is given by (Eq. 8, Ref. 1)

$$E = E^{\mathrm{LSDA}} + \frac{1}{2}\sum_{t,\sigma}\sum_{ijkl}\langle\chi_i^t;\chi_k^t|V_{ee}|\chi_j^t;\chi_l^t\rangle n_{ij}^{t,\sigma}n_{kl}^{t,-\sigma} + \frac{1}{2}\sum_{t,\sigma}\sum_{ijkl}\Bigg(\langle\chi_i^t;\chi_k^t|V_{ee}|\chi_j^t;\chi_l^t\rangle - \langle\chi_i^t;\chi_k^t|V_{ee}|\chi_l^t;\chi_j^t\rangle\Bigg)n_{ij}^{t,\sigma}n_{kl}^{t,\sigma} - \sum_t\left[\frac{U}{2}\sum_{\sigma\sigma'}N^{t,\sigma}(N^{t,\sigma'}-\delta_{\sigma,\sigma'}) - \frac{J}{2}\sum_{\sigma}N^{t\sigma}(N^{t,\sigma}-1)\right]. \tag{1}$$

Here t labels the atomic site (position of Mn nucleus in our case), σ is the electron spin, and i, j, k, and l are the azimuthal angular momentum numbers within the $l = 2$ or d shell. The four-center integrals $\langle\chi_i^t;\chi_k^t|V_{ee}|\chi_j^t;\chi_l^t\rangle$ are the matrix elements of the screened coulomb interaction $V_{ee}(r,r')$ (see below).

The "d-orbital occupancies" $n_{mm'}^{t,\sigma}$ are given by

$$n_{mm'}^{t,\sigma} = \sum_{n\mathbf{k}} f_{n\mathbf{k}}^{\sigma}\langle\Psi_n^{\mathbf{k}\sigma}|P_{m,m'}^t|\Psi_n^{\mathbf{k}\sigma}\rangle\,, \tag{2}$$

where $|\Psi_n^{\mathbf{k}\sigma}\rangle$ is the pseudo wavefunction defined within the PAW formalism,[1,2] $f_{n\mathbf{k}}^{\sigma}$ is the Fermi distribution, and n and $\mathbf{k}$ index the occupied electron band and the Brillouin zone. The projector $P_{m,m'}^t$, centered on atomic nucleus t at position $\mathbf{R}_t$, is defined as

$$P_{m,m'}^t(\mathbf{r},\mathbf{r}') = \theta_{\Omega_t}(\mathbf{r})\delta(|\mathbf{r}'-\mathbf{R}_t| - |\mathbf{r}-\mathbf{R}_t|)Y_{l,m}(\hat{\mathbf{r}})Y_{l,m'}^*(\hat{\mathbf{r}}')\,, \tag{3}$$

where $Y_{l,m}(\hat{\mathbf{r}})$ are spherical harmonics with $l = 2$ and azimuthal angular momentum number m. The Heaviside function $\theta_{\Omega_t}(\mathbf{r}) = 1$ for $|\mathbf{r}-\mathbf{R}_t| < r_c^t$ and is zero otherwise. r_c^t is determined by the PAW wavefunctions created for a particular element (in our case, Mn). As such, this implementation is technically not "basis-set independent."[3] However, we emphasize that we fix $J = 1$ eV and fit our U parameter to B3LYP spin splittings. Any slight basis set difference will be partially compensated by this procedure.

$N^{t,\sigma} = \sum_i n_{ii}^{t,\sigma}$ is the average occupation of the d shell on atom t for each spin direction σ.

The d-orbital wavefunction with azimuthal angular momentum number m centered on atom t is assumed to take the form of orbitals on isolated atoms,

$$\chi_m^t(\mathbf{r}) = \chi_d(|\mathbf{r}-\mathbf{R}_t|)Y_{l=2,m}(\hat{\mathbf{r}}-\mathbf{R}_t)\,. \tag{4}$$

Within the DFT+U formulation, $\chi_d(r)$ and the matrix elements $\langle\chi_i^t;\chi_k^t|V_{ee}|\chi_j^t;\chi_l^t\rangle$ are not computed explicitly; instead, taking advantage of the spherical harmonics characteristics of $|\chi_i^t\rangle$, and making the assumption of spatially homogeneous dielectric screening, the 4-center integrals in Eq. 1 are expressed in terms of "screened Slater integrals" and related to the parameters U and J, which are the Coulomb self-energy and the exchange parameter, respectively.[1] U and J are thus *identified* as the averages (Eqs. 18 & 19 of Ref. 1),

$$U = \frac{1}{(2l+1)^2}\sum_{mm'}\langle\chi_m^t;\chi_{m'}^t|V_{ee}|\chi_m^t;\chi_{m'}^t\rangle \tag{5}$$

$$J = \frac{1}{(2l)(2l+1)}\sum_{m\neq m',m'}\langle\chi_m^t;\chi_{m'}^t|V_{ee}|\chi_{m'}^t;\chi_m^t\rangle\,, \tag{6}$$

and used as parameters in the DFT+U calculations.

VASP DFT+U calculations are performed self-consistently.[4] In other words, a self-consistent spin-polarized GGA calculation is performed using the PAW method. Then Hubbard correction (Eq. 1) is added to the GGA "Hamiltonian," and the new Hamiltonian is iterated until the occupation numbers $n^{t,\sigma}_{mm'}$ have converged.[3] Then, the spin-polarized PBE potential is updated when the Hubbard correction (Eq. 1) is added to the GGA "Hamiltonian," and the procedure is repeated until convergence is achieved.[4] In our geometry relaxation calculations, we find that the total energy is indeed minimized where the forces become small—just as one would expect with full self-consistency. Note that earlier VASP DFT+U work did not update the GGA Hamiltonian after addition of the Hubbard correction.[3] Bengone *et al.* reported[3] that the so-called second-variation procedure for self-consistent DFT+U,[5] in which the spin-polarized GGA potential is updated, did not yield much improvement over calculations without such updates, consistent with previous investigations.[5]

2: Atomic coordinates for PdP adsorbed edgewise on Au(111)

Tables 1–3 list the optimal coordinates computed using the SeqQuest[6] code and the LDA exchange correlation functional. Coordinates are listed for an Au(111) slab, a palladium porphine (PdP) molecule, and the composite PdP adsorbed edgewise on Au(111) system. The simulation cell has dimensions 5.75×14.95×27 Å^3. Coordinates and lattice constants computed using the VASP[7] code with LDA exchange correlation functional are similar. Note that the periodic boundary conditions in the x direction means that the PdP molecules are in reality in a "stack-like" geometry with repeating units 5.75 Å apart, similar to Ref. 3. Despite this separation distance, it is found that a 4×2×1 Brillouin zone sampling is needed for energy convergence. The LDA adsorption energy obtained between the PdP "stack" and the Au(111) slab is 0.25 eV. (In contrast, with the PBE[9] exchange correlation functional, there is little or no binding energy, similar to that found for PdP adsorption on Al(111).[10])

3: Normal-Coordinate Structural Decomposition

Tables 4–13 list the Normal-coordinate Structural Decomposition (NSD)[11] analyses of metal porphyrin crystal structures taken from the literature as well as some DFT and DFT+U predicted structures from this work. All deformations are in Angstroms.

4: Gaussian 03 complete citation

The complete citation is given in Ref. 12.

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atom	x	y	z	atom	x	y	z
Au	0.0000	0.0000	0.0000	Au	0.0000	3.3266	2.3574
Au	2.8764	0.0000	0.0000	Au	2.8764	3.3266	2.3574
Au	0.0000	4.9822	0.0000	Au	0.0000	8.3087	2.3574
Au	2.8764	4.9822	0.0000	Au	2.8764	8.3087	2.3574
Au	0.0000	9.9643	0.0000	Au	0.0000	13.2909	2.3574
Au	2.8764	9.9643	0.0000	Au	2.8764	13.2909	2.3574
Au	1.4382	2.4911	0.0000	Au	0.0000	1.6556	-2.3574
Au	4.3146	2.4911	0.0000	Au	2.8764	1.6556	-2.3574
Au	1.4382	7.4732	0.0000	Au	0.0000	6.6378	-2.3574
Au	4.3146	7.4732	0.0000	Au	2.8764	6.6378	-2.3574
Au	1.4382	12.4554	0.0000	Au	0.0000	11.6199	-2.3574
Au	4.3146	12.4554	0.0000	Au	2.8764	11.6199	-2.3574
Au	1.4382	0.8355	2.3574	Au	1.4382	4.1467	-2.3574
Au	4.3146	0.8355	2.3574	Au	4.3146	4.1467	-2.3574
Au	1.4382	5.8176	2.3574	Au	1.4382	9.1288	-2.3574
Au	4.3146	5.8176	2.3574	Au	4.3146	9.1288	-2.3574
Au	1.4382	10.7998	2.3574	Au	1.4382	14.1110	-2.3574
Au	4.3146	10.7998	2.3574	Au	4.3146	14.1110	-2.3574

TABLE 1: Atomic coordinates (in Å) for a 3-layer Au(111) slab.

atom	x	y	z	atom	x	y	z
C	0.0000	-0.6757	-4.1819	N	0.0000	-1.9982	0.0000
C	0.0000	-0.6756	4.1820	N	0.0000	0.0000	-1.9977
C	0.0000	-1.0944	-2.8181	N	0.0000	0.0000	1.9977
C	0.0000	-1.0944	2.8181	N	0.0000	1.9982	0.0000
C	0.0000	-2.4032	-2.4029	H	0.0000	-1.3556	-5.0320
C	0.0000	-2.4032	2.4029	H	0.0000	-1.3556	5.0320
C	0.0000	-2.8189	-1.0943	H	0.0000	-3.1754	-3.1755
C	0.0000	-2.8189	1.0943	H	0.0000	-3.1754	3.1755
C	0.0000	-4.1827	-0.6756	H	0.0000	-5.0329	-1.3554
C	0.0000	-4.1827	0.6756	H	0.0000	-5.0329	1.3554
C	0.0000	0.6756	-4.1819	H	0.0000	1.3556	-5.0320
C	0.0000	0.6757	4.1820	H	0.0000	1.3556	5.0320
C	0.0000	1.0944	-2.8181	H	0.0000	3.1754	-3.1755
C	0.0000	1.0944	2.8181	H	0.0000	3.1754	3.1755
C	0.0000	2.4032	-2.4029	H	0.0000	5.0329	-1.3554
C	0.0000	2.4032	2.4029	H	0.0000	5.0329	1.3554
C	0.0000	2.8189	-1.0943	Pd	0.0000	0.0000	0.0000
C	0.0000	2.8189	1.0943				
C	0.0000	4.1827	-0.6756				
C	0.0000	4.1827	0.6756				

TABLE 2: Atomic coordinates (in Å) for PdP in stack geometry in the unit cell.

atom	x	y	z	atom	x	y	z	atom	x	y	z
Au	-3.1139	-6.9210	-7.1320	Au	-1.6714	-6.0797	-4.7750	Au	-0.2339	-5.2472	-2.4129
Au	-0.2317	-6.9210	-7.1320	Au	1.2047	-6.0779	-4.7730	Au	-3.1086	-5.2482	-2.4142
Au	-1.6728	-4.4250	-7.1320	Au	-0.2350	-3.5921	-4.7845	Au	1.2055	-2.7715	-2.4481
Au	1.2094	-4.4250	-7.1320	Au	-3.1070	-3.5905	-4.7831	Au	-1.6716	-2.7615	-2.4202
Au	-0.2317	-1.9289	-7.1320	Au	1.2042	-1.0928	-4.7807	Au	-3.0933	-0.2595	-2.4542
Au	-3.1139	-1.9289	-7.1320	Au	-1.6703	-1.1047	-4.7904	Au	-0.2501	-0.2598	-2.4473
Au	1.2094	0.5671	-7.1320	Au	-3.1063	1.4036	-4.7858	Au	-1.6714	2.2425	-2.4192
Au	-1.6728	0.5671	-7.1320	Au	-0.2355	1.4016	-4.7846	Au	1.2067	2.2511	-2.4591
Au	-3.1139	3.0631	-7.1320	Au	-1.6712	3.8948	-4.7768	Au	-0.2336	4.7271	-2.4107
Au	-0.2317	3.0631	-7.1320	Au	1.2043	3.9042	-4.7852	Au	-3.1084	4.7277	-2.4120
Au	-1.6728	5.5592	-7.1320	Au	-0.2336	6.3808	-4.7683	Au	1.2050	7.2138	-2.4106
Au	1.2094	5.5592	-7.1320	C	1.0196	-1.2402	1.8458				
C	0.8872	-1.2451	7.4646	C	0.9969	-2.5534	2.2450	C	0.8730	-2.5543	7.0474
C	0.9354	-2.9707	3.5506	C	0.8794	-2.9698	5.7389	C	0.9088	-4.3339	3.9676
C	0.8733	-4.3333	5.3180	C	1.0956	0.5355	0.4937	C	0.8938	0.5247	8.8292
C	0.9888	0.9514	1.8484	C	0.8883	0.9453	7.4660	C	0.9376	2.2635	2.2497
C	0.8672	2.2550	7.0520	C	0.8817	2.6788	3.5560	C	0.8566	2.6735	5.7438
C	0.8429	4.0412	3.9758	C	0.8284	4.0375	5.3265	N	0.9110	-2.1485	4.6452
N	0.9553	-0.1457	2.6653	N	0.8891	-0.1497	6.6456	N	0.8833	1.8543	4.6490
H	1.2118	-1.5062	-0.3568	H	0.8924	-1.5054	9.6792	H	1.0350	-3.3165	1.4633
H	0.8586	-3.3277	7.8193	H	0.9184	-5.1840	3.2877	H	0.8474	-5.1849	5.9952
H	1.1711	1.2276	-0.3530	H	0.8957	1.2018	9.6810	H	0.9519	3.0273	1.4675
H	0.8552	3.0266	7.8260	H	0.8329	4.8931	3.2982	H	0.8024	4.8877	6.0059
Pd	0.9058	-0.1473	4.6510								

TABLE 3: Atomic coordinates (in Å) for PdP adsorbed edgewise on Au(111).

TABLE 4: NSD results for the PBE structure of PdP.

basis	Dip	dip	B2g	B1g	Eu(x)	Eu(y)	A1g	A2g
min.	0.1527	0.0049	0.0000	0.0000	-0.0000	-0.0000	0.1527	0.0000
ext.	0.1530	0.0048	0.0000	0.0000	-0.0000	-0.0000	0.1535	0.0000
			-0.0000	-0.0000	-0.0001	-0.0000	-0.0098	-0.0000
			0.0000	0.0000	-0.0000	0.0000	0.0166	0.0000
			0.0000	-0.0000	-0.0001	0.0000	0.0161	-0.0000
			-0.0000	0.0000	-0.0000	-0.0000	-0.0023	-0.0000
			-0.0000	-0.0000	0.0000	-0.0000	0.0053	
					-0.0001	0.0000		
					-0.0000	-0.0000		
					0.0000	0.0000		
					0.0000	0.0000		
					0.0000	-0.0000		
comp.	0.1549	0.0000	0.0000	0.0000	0.0001	0.0001	0.1549	0.0001

basis	Doop	doop	B2u	B1u	A2u	Eg(x)	Eg(y)	A1u
min.	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0000	0.0000
ext.	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0000	0.0000
			0.0000	-0.0000	-0.0000	0.0000	-0.0000	-0.0000
			-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	
						0.0000	-0.0000	
						-0.0000	-0.0000	
comp.	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Pd-N = 2.035 Å

TABLE 5: NSD results for the crystal structure of PdTPP (CCDC refcode PDTPOR).

Reference:
E. B. Fleischer, C. K. Miller, L. E. Webb (1964) *J. Am. Chem. Soc.,* **86,** 2342.

basis	Dip	dip	B2g	B1g	Eu(x)	Eu(y)	A1g	A2g
min.	0.0135	0.0193	0.0000	-0.0000	-0.0000	-0.0000	-0.0134	-0.0011
ext.	0.0700	0.0142	0.0000	0.0000	-0.0000	-0.0000	-0.0116	-0.0026
			0.0000	0.0000	-0.0000	0.0000	0.0524	-0.0449
			-0.0000	0.0000	-0.0000	-0.0000	0.0345	-0.0209
			0.0000	0.0000	0.0000	-0.0000	-0.0544	-0.0152
			0.0000	0.0000	0.0000	0.0000	0.0021	0.0233
			-0.0000	0.0000	-0.0000	-0.0000	0.0158	
					-0.0000	-0.0000		
					-0.0000	0.0000		
					0.0000	0.0000		
					0.0000	-0.0000		
					-0.0000	-0.0000		
comp.	0.1026	0.0000	0.0000	0.0000	0.0000	0.0000	0.0855	0.0567
basis	Doop	doop	B2u	B1u	A2u	Eg(x)	Eg(y)	A1u
min.	1.0979	0.0276	-0.2020	1.0791	0.0000	-0.0000	-0.0000	-0.0000
ext.	1.1080	0.0083	-0.1998	1.0791	0.0000	-0.0000	-0.0000	-0.0000
			0.1450	0.0226	0.0000	0.0000	-0.0000	0.0000
			-0.0418	-0.0286	-0.0000	0.0000	0.0000	
						0.0000	-0.0000	
						-0.0000	0.0000	
comp.	1.1092	0.0000	0.2538	1.0798	0.0000	0.0000	0.0000	0.0000

Pd-N = 2.010 Å

TABLE 6: NSD results for the crystal structure of PdOEP (CCDC refcode QARPUU).

Reference:
T. Ishii, N. Aizawa, M. Yamashita, H. Matsuzaka, T. Kodama, K. Kikuchi, I. Ikemoto, Y. Iwasa (2000) *J. Chem. Soc., Dalton Trans.,* 4407.

Molecule 1 containing Pd(1).

basis	Dip	dip	B2g	B1g	Eu(x)	Eu(y)	A1g	A2g
min.	0.0414	0.0374	0.0223	-0.0267	-0.0010	0.0155	0.0097	-0.0128
ext.	0.0882	0.0342	0.0204	-0.0248	-0.0017	0.0175	0.0120	-0.0133
			-0.0495	-0.0424	0.0144	-0.0001	0.0352	-0.0148
			-0.0078	0.0454	0.0158	-0.0043	0.0360	0.0083
			-0.0307	0.0122	0.0325	-0.0102	0.0274	-0.0164
			0.0333	0.0269	-0.0076	0.0504	0.0099	-0.0128
			0.0047	0.0044	-0.0465	0.0215	-0.0026	
					0.0707	0.0282		
					0.0271	0.0124		
					-0.0682	-0.0055		
					0.0127	0.0229		
					-0.0491	-0.0677		
comp.	0.2030	0.0000	0.0712	0.0741	0.1300	0.0972	0.0584	0.0298

basis	Doop	doop	B2u	B1u	A2u	Eg(x)	Eg(y)	A1u
min.	0.6750	0.0105	0.0007	0.6707	-0.0667	-0.0064	0.0275	-0.0242
ext.	0.6753	0.0093	0.0008	0.6707	-0.0682	-0.0069	0.0274	-0.0242
			0.0037	-0.0134	-0.0145	-0.0015	0.0014	-0.0031
			0.0030	0.0256	-0.0190	-0.0408	0.0083	
						-0.0211	-0.0023	
						0.0141	-0.0106	
comp.	0.6779	0.0000	0.0046	0.6713	0.0707	0.0486	0.0308	0.0244

Pd(1)-N = 2.018 Å (2.033, 2.042, 1.982, 2.103)

TABLE 7: NSD results for the DFT+U structure of MnP.

basis	Dip	dip	B2g	B1g	Eu(x)	Eu(y)	A1g	A2g
min.	0.3631	0.0080	0.0000	0.0000	0.0000	0.0000	0.3631	-0.0000
ext.	0.3632	0.0081	0.0000	0.0000	0.0000	0.0000	0.3656	-0.0000
			0.0000	0.0000	-0.0000	-0.0000	0.0111	0.0000
			0.0000	0.0000	-0.0000	-0.0000	0.0466	0.0000
			-0.0000	-0.0000	0.0000	0.0000	0.0125	0.0000
			0.0000	-0.0000	-0.0000	-0.0000	0.0042	0.0000
			-0.0000	0.0000	0.0000	0.0000	0.0010	
					-0.0000	-0.0000		
					-0.0000	-0.0000		
					-0.0000	-0.0000		
					-0.0000	-0.0000		
					0.0000	0.0000		
comp.	0.3664	0.0000	0.0000	0.0000	0.0000	0.0000	0.3664	0.0000

basis	Doop	doop	B2u	B1u	A2u	Eg(x)	Eg(y)	A1u
min.	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ext.	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
			0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
			0.0000	0.0000	0.0000	0.0000	0.0000	
						0.0000	0.0000	
						0.0000	0.0000	
comp.	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Mn-N = 2.090 Å

TABLE 8: NSD results for the crystal structure of MnTPP (CCDC refcode TPPMNT).

Reference:
J.F. Kirner, C.A. Reed, W.R. Scheidt (1977) *J. Am. Chem. Soc.,* **99,** 1093

basis	Dip	dip	B2g	B1g	Eu(x)	Eu(y)	A1g	A2g
min.	0.3341	0.0086	0.0106	0.0340	0.0000	0.0000	0.3322	0.0023
ext.	0.3349	0.0075	0.0108	0.0336	0.0000	0.0000	0.3345	0.0022
			0.0086	-0.0015	-0.0000	-0.0000	-0.0213	0.0003
			-0.0019	-0.0102	0.0000	0.0000	0.0404	-0.0010
			0.0037	-0.0016	-0.0000	0.0000	0.0009	0.0004
			-0.0056	0.0068	0.0000	-0.0000	0.0165	-0.0004
			-0.0017	-0.0018	0.0000	0.0000	-0.0085	
					-0.0000	0.0000		
					0.0000	0.0000		
					0.0000	0.0000		
					0.0000	0.0000		
					0.0000	0.0000		
comp.	0.3381	0.0000	0.0155	0.0362	0.0000	0.0000	0.3357	0.0026

basis	Doop	doop	B2u	B1u	A2u	Eg(x)	Eg(y)	A1u
min.	0.3193	0.0206	0.0000	0.0000	-0.0000	-0.0640	0.3128	0.0000
ext.	0.3416	0.0041	0.0000	0.0000	-0.0000	-0.0653	0.3176	0.0000
			0.0000	0.0000	0.0000	-0.0323	0.1180	0.0000
			0.0000	-0.0000	0.0000	0.0002	-0.0027	
						-0.0104	-0.0042	
						0.0024	0.0207	
comp.	0.3424	0.0000	0.0000	0.0000	0.0000	0.0725	0.3347	0.0000

Mn-N = 2.085 Å (2.083, 2.086)

TABLE 9: NSD results for the DFT+U structure of MnClP.

basis	Dip	dip	B2g	B1g	Eu(x)	Eu(y)	A1g	A2g
min.	0.1132	0.0057	-0.0060	-0.0000	0.0001	0.0001	0.1131	-0.0000
ext.	0.1148	0.0041	-0.0059	-0.0000	0.0001	0.0001	0.1138	-0.0000
			0.0005	-0.0000	0.0003	0.0003	-0.0188	0.0000
			0.0004	0.0000	-0.0000	-0.0000	0.0124	0.0000
			0.0003	-0.0000	0.0002	0.0002	0.0162	-0.0000
			0.0004	-0.0000	0.0000	0.0000	0.0024	0.0000
			0.0015	-0.0000	0.0000	0.0000	0.0017	
					0.0001	0.0001		
					-0.0005	-0.0005		
					0.0000	0.0000		
					-0.0001	-0.0001		
					-0.0002	-0.0002		
comp.	0.1166	0.0000	0.0062	0.0000	0.0007	0.0007	0.1164	0.0000
basis	Doop	doop	B2u	B1u	A2u	Eg(x)	Eg(y)	A1u
min.	0.0180	0.0026	0.0000	0.0027	0.0178	0.0003	0.0003	0.0000
ext.	0.0245	0.0002	0.0000	0.0027	0.0185	0.0003	0.0003	0.0000
			0.0000	0.0008	0.0167	-0.0000	-0.0000	0.0000
			-0.0000	-0.0009	0.0002	0.0001	0.0001	
						0.0002	0.0002	
						-0.0005	-0.0005	
comp.	0.0245	0.0000	0.0000	0.0029	0.0243	0.0006	0.0006	0.0000

Mn-N = 2.045 Å

TABLE 10: NSD results for the crystal structure of MnClTPP (CCDC refcode HIFMIS).

Reference:
B. Cheng, W. R. Scheidt (1996) *Acta Crystallogr., Sect.C: Cryst. Struct. Commun.,* **52,** 361.

basis	Dip	dip	B2g	B1g	Eu(x)	Eu(y)	A1g	A2g
min.	0.0149	0.0124	0.0000	0.0000	-0.0000	0.0000	-0.0135	0.0063
ext.	0.0560	0.0069	0.0000	0.0000	-0.0000	0.0000	-0.0135	0.0059
			0.0000	0.0000	-0.0000	0.0000	-0.0536	0.0063
			-0.0000	0.0000	-0.0000	0.0000	0.0125	-0.0064
			0.0000	0.0000	-0.0000	0.0000	-0.0258	-0.0004
			0.0000	0.0000	-0.0000	-0.0000	-0.0180	-0.0052
			0.0000	0.0000	-0.0000	0.0000	0.0139	
					0.0000	0.0000		
					-0.0000	0.0000		
					-0.0000	-0.0000		
					-0.0000	0.0000		
					-0.0000	-0.0000		
comp.	0.0676	0.0000	0.0000	0.0000	0.0000	0.0000	0.0665	0.0121

basis	Doop	doop	B2u	B1u	A2u	Eg(x)	Eg(y)	A1u
min.	0.0000	0.0000	-0.0000	-0.0000	-0.0000	-0.0000	0.0000	-0.0000
ext.	0.0000	0.0000	-0.0000	-0.0000	-0.0000	-0.0000	0.0000	-0.0000
			-0.0000	0.0000	-0.0000	-0.0000	0.0000	-0.0000
			-0.0000	0.0000	-0.0000	-0.0000	-0.0000	
						-0.0000	-0.0000	
						0.0000	-0.0000	
comp.	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Mn-N = 2.001 Å

TABLE 11: NSD results for the DFT+U structure of MnP on Au.

basis	Dip	dip	B2g	B1g	Eu(x)	Eu(y)	A1g	A2g
min.	0.0853	0.0084	-0.0009	0.0002	-0.0010	0.0001	0.0853	0.0009
ext.	0.0921	0.0049	-0.0010	0.0002	-0.0010	0.0000	0.0847	0.0009
			0.0011	0.0002	0.0021	-0.0001	-0.0346	-0.0010
			-0.0000	-0.0006	0.0006	0.0001	-0.0008	0.0003
			-0.0010	0.0000	0.0003	-0.0000	0.0172	-0.0004
			-0.0010	-0.0006	-0.0001	0.0002	-0.0162	-0.0001
			-0.0015	-0.0001	-0.0004	-0.0002	-0.0063	
					0.0001	-0.0003		
					-0.0001	-0.0007		
					-0.0000	0.0004		
					-0.0007	-0.0003		
					-0.0001	-0.0001		
comp.	0.0953	0.0000	0.0025	0.0008	0.0026	0.0010	0.0952	0.0014

basis	Doop	doop	B2u	B1u	A2u	Eg(x)	Eg(y)	A1u
min.	0.1020	0.0040	0.0511	-0.0285	0.0835	-0.0015	0.0034	0.0015
ext.	0.1055	0.0010	0.0511	-0.0285	0.0826	-0.0013	0.0033	0.0015
			-0.0023	0.0084	-0.0243	0.0043	-0.0044	0.0000
			-0.0004	0.0044	0.0048	0.0001	-0.0004	
						0.0002	-0.0001	
						0.0004	0.0001	
comp.	0.1057	0.0000	0.0512	0.0300	0.0871	0.0046	0.0056	0.0015

Mn-N = 2.022 Å

TABLE 12: NSD results for the DFT+U structure of MnP on Au with an electric field of 0.7.

basis	Dip	dip	B2g	B1g	Eu(x)	Eu(y)	A1g	A2g
min.	0.3116	0.0061	0.0087	0.0029	0.0005	-0.0015	0.3115	0.0009
ext.	0.3121	0.0047	0.0087	0.0029	0.0005	-0.0015	0.3131	0.0009
			-0.0002	-0.0009	-0.0006	-0.0019	0.0170	-0.0007
			0.0007	-0.0006	-0.0002	0.0000	0.0266	-0.0010
			0.0002	-0.0002	-0.0007	0.0006	0.0117	-0.0007
			0.0003	0.0009	0.0006	-0.0006	0.0084	-0.0000
			-0.0003	0.0004	0.0002	-0.0001	-0.0053	
					-0.0002	0.0004		
					-0.0003	0.0003		
					-0.0003	-0.0003		
					-0.0000	-0.0006		
					-0.0006	-0.0001		
comp.	0.3136	0.0000	0.0087	0.0033	0.0015	0.0027	0.3134	0.0017
basis	Doop	doop	B2u	B1u	A2u	Eg(x)	Eg(y)	A1u
min.	0.0377	0.0023	0.0198	0.0053	0.0291	-0.0078	0.0097	0.0020
ext.	0.0394	0.0019	0.0197	0.0053	0.0290	-0.0078	0.0097	0.0020
			-0.0013	0.0006	0.0105	0.0026	-0.0013	-0.0010
			0.0001	0.0011	-0.0105	-0.0014	-0.0000	
						-0.0000	-0.0000	
						-0.0011	0.0013	
comp.	0.0408	0.0000	0.0198	0.0054	0.0327	0.0084	0.0099	0.0022

Mn-N = 2.156

TABLE 13: NSD results for the crystal structure of NiP (CCDC refcode TEMKOL).

Reference: W. Jentzen, I. Turowska-Tyrk, W. R. Scheidt, J. A. Shelnutt (1996) *Inorg.Chem.,* **35,** 3559.

basis	Dip	dip	B2g	B1g	Eu(x)	Eu(y)	A1g	A2g
min.	0.1577	0.0078	0.0069	-0.0099	0.0069	0.0045	-0.1571	0.0014
ext.	0.1588	0.0069	0.0069	-0.0096	0.0068	0.0045	-0.1591	0.0013
			-0.0069	0.0027	0.0056	0.0065	-0.0145	0.0025
			-0.0003	0.0043	-0.0033	-0.0008	-0.0323	0.0001
			0.0013	-0.0007	0.0035	-0.0015	0.0057	-0.0007
			0.0031	0.0033	-0.0024	-0.0011	-0.0193	-0.0033
			-0.0006	0.0016	0.0017	0.0014	0.0087	
					0.0035	0.0019		
					-0.0007	-0.0013		
					0.0013	0.0011		
					-0.0014	-0.0004		
					0.0008	0.0022		
comp.	0.1638	0.0000	0.0104	0.0116	0.0113	0.0090	0.1623	0.0044

basis	Doop	doop	B2u	B1u	A2u	Eg(x)	Eg(y)	A1u
min.	0.0871	0.0059	-0.0129	0.0791	0.0061	0.0332	-0.0032	0.0035
ext.	0.0932	0.0018	-0.0131	0.0791	0.0059	0.0321	-0.0031	0.0035
			-0.0077	0.0028	-0.0057	-0.0310	0.0045	0.0018
			0.0000	0.0039	0.0028	0.0053	-0.0078	
						0.0015	0.0002	
						0.0010	0.0007	
comp.	0.0938	0.0000	0.0150	0.0793	0.0089	0.0459	0.0097	0.0039

Ni-N = 1.951 Å (1.948, 1.950, 1.953, 1.952)