Appendix B

Energy levels of group 10 transition metal atoms and ions

B.1 Abstract

The energies of the group 10 transition metals (Ni, Pd, and Pt) in different configurations (d^8s^2, d^9s^1, and d^{10}) are calculated using various DFT methods. Furthermore, energies of the corresponding 1+ and 2+ ions are also calculated. The results of the various DFT methods are compared with the experimental energies [1] and previous calculations [2], with the purpose of determining the best DFT method for each atom. Finally, inconsistent energies in supposedly degenerate orbitals of the ionic states are observed and a potential solution is proposed.

Table B.1. Relativistic *vs.* nonrelativistic Hartree-Fock excitation energies, taken from Martin and Hay [2].

Atom	Config.	Hartree Fock	Relativistic HF	Experimental
Nickel	d^8s^2	0.00	0.00	0.00
	d^9s^1	1.27	1.63	−0.03
	d^{10}	5.47	6.04	1.71
Palladium	d^8s^2	0.00	0.00	0.00
	d^9s^1	−3.01	−2.09	−2.43
	d^{10}	−3.76	−2.19	−3.38
Platinum	d^8s^2	0.00	0.00	0.00
	d^9s^1	−3.28	−0.40	−0.64
	d^{10}	−4.69	0.50	−0.16

Relative energies in eV. The experimental energies are averages over spin-orbit components [1].

B.2 Introduction

Density function theory has found widespread application in computational chemistry as a fast alternative to *ab initio* calculations with correlation. However, the accuracy of DFT calculations is sometimes called into question in many transition metal-containing systems, due to the fact that transition metals often have several closely-spaced low-lying energy levels and that DFT is not always able to predict the correct ground state. In this report we present the results of calculations of the levels of Ni, Pd, and Pt with the following DFTs: B3LYP, M06, M06-2X, M06-HF, M06-L, PBE, PBE0, and XYGJ-OS (Ni only); and we contrast these with a few electron-correlation calculations, including HF, MP2, and CCSD, and with previous calculations done by Martin and Hay [2].

B.3 The neutral atom

The group 10 transition metals are notable in that each atom in the column has a different ground state electron configuration, *viz.* d^8s^2 for Ni, d^{10} for Pd, and d^9s^1 for Pt. While Ni conforms to the Aufbau principle, Pd and Pt do not. This is due to a complex interplay of electron correlation and relativistic effects. The ordering of the ground and excited states of Pd and Pt have long been known (Table B.1), but the identity of the ground state of Ni has been somewhat more contentious [3].

There are a few observations to note in Table B.1. First, the experimentally determined ground state of Ni is $d^8s^2\ {}^3F_4$, but the energies in Table B.1 are averages over all $J = 2, 3, 4$, which in the case of Ni results in an energy that is slightly higher than the ${}^3P$ average. Secondly, we find that relativistic corrections, though unnecessary for Ni, become important for Pd and absolutely vital for Pt. Finally, we find that the Hartree-Fock calculations do a poor job of ordering the configurations

Table B.2. Relativistic *vs.* nonrelativistic Hartree-Fock excitation energies for the M$^+$ ions [2].

Atom	Config.	Hartree Fock	Relativistic HF	Experimental
Nickel	d^8s^2	0.00	0.00	0.00
Ni$^+$	d^9	7.61	8.12	7.59
	d^8s^1	6.98	7.09	8.67
Palladium	d^8s^2	0.00	0.00	0.00
Pd$^+$	d^9	2.91	4.25	5.13
	d^8s^1	6.36	6.66	8.32
Platinum	d^8s^2	0.00	0.00	0.00
Pt$^+$	d^9	2.68	7.26	8.46
	d^8s^1	6.26	7.51	9.22

Relative energies in eV.

Table B.3. Excitation energies of Pt atom as calculated by various DFTs.

Config.	Exp.	HF	B3LYP	M06	M06-2X	M06-HF	M06-L	PBE	PBE0
d^9s^1		−118.23	−119.08	−119.03	−118.95	−118.91	−119.08	−119.07	−119.04
d^{10}	11.07	25.41	14.67	0.40	11.72	24.95	14.01	14.39	15.03
d^8s^2	14.76	5.95	6.84	19.17	15.24	21.07	0.86	−0.05	9.08

The d^9s^1 row contains the absolute energies in hartrees. The other rows contain the energies relative to the d^9s^1 ground state, in kcal/mol. Experimental energies derived from Moore [1]. Color coding represents deviation from experimental value. Gray: within 1 kcal/mol; blue: within 5 kcal/mol; green: within 10 kcal/mol; yellow: within 15 kcal/mol.

for the Pt atom. Hence, the first part of this report shall many focus on DFT calculations of the Pt atom, with additional data for Ni and Pd for purposes of comparison.

We also examine the previously-calculated excitation energies for the singly-charged cations Ni$^+$, Pd$^+$, and Pt$^+$. These numbers are taken from the same reference [2] and are reproduced in Table B.2.

Looking at the values in Table B.2, two things are apparent: First, the numbers for Ni$^+$, while close, are in the wrong order, putting the d^8s^1 configuration below the d^9 configuration in energy. And secondly, while the HF calculations for Pd$^+$ and Pt$^+$ give the correct ground state configuration, the relative energies are significantly off. This report will also give updated excitation energy calculations for the singly-charged cations.

B.3.1 Platinum (0)

Calculations with Pt were performed on Jaguar version 7.5 [4]. The basis set used was a variant of LACV3P**++, modified to include f functions [5]. The results are presented in Table B.3.

Table B.4. Excitation energies of Pt atom calculated without f functions.

Config.	Exp.	HF	B3LYP	M06	M06-2X	M06-HF	M06-L	PBE	PBE0
d^9s^1		−118.23	−119.08	−119.03	−118.95	−118.91	−119.08	−119.07	−119.04
d^{10}	11.07	27.96	14.67	0.40	11.72	24.95	14.01	14.43	15.03
d^8s^2	14.76	1.41	5.10	12.22	15.04	21.11	6.99	0.02	8.24
$\delta\delta$ (a)		30.24	28.38	26.43	31.96	39.30	32.84	29.52	30.94
$\pi\pi$ (b)		8.50	12.77	19.62	19.46	30.11	16.22	15.22	15.26
$\sigma\delta$ (c)	14.76	1.25	7.57	17.36	15.30	27.04	10.68	10.50	10.03

The d^9s^1 row contains the absolute energies in hartrees. The other rows contain the energies relative to the d^9s^1 ground state, in kcal/mol. Experimental energies derived from Moore [1]. Color coding represents deviation from experimental value. Gray: within 1 kcal/mol; blue: within 5 kcal/mol; green: within 10 kcal/mol; yellow: within 15 kcal/mol.

(a) Energy of the d^8s^2 configuration with singly occupied d_{xy} and $d_{x^2-y^2}$ orbitals.

(b) Energy of the d^8s^2 configuration with singly occupied d_{xz} and d_{yz} orbitals.

(c) Extrapolated energy of the ground d^8s^2 configuration according to the formula $E_{\sigma\delta} = \frac{4}{3}E_{\pi\pi} - \frac{1}{3}E_{\delta\delta}$.

An examination of the data presented in Table B.3 shows that while most DFT methods are very good at predicting the $d^9s^1 - d^{10}$ separation, they are considerably poorer at correctly ordering the d^8s^2 state, often putting it near the d^9s^1 state instead of above the d^{10} state. An examination of the molecular orbitals in the d^8s^2 output files in Molden revealed considerable mixing of the d and s orbitals in some of the cases. Hence, the true configuration, d^9s^1 or d^8s^2, could not be ascertained, and hence the values could not be trusted.

In order to prevent this catastrophic mixing of orbitals, the input files for the d^8s^2 cases were rerun with the symmetry turned on (Table B.4, row 3). This prevented the basis set from using the added f functions. Fortunately, an examination of the rerun numbers for the d^9s^1 and d^{10} cases (Table B.4, rows 1-2) showed that the f functions play a very minor role in the total energy and hence can be safely ignored.

Unfortunately, examination of the molecular orbitals in the d^8s^2 output files in Molden revealed that there was still some mixing between the filled s orbital and the empty d_{z^2} orbital among the β electrons. This is due to both orbitals being totally symmetric in the point group used for the calculations (D_{4h} or its largest Abelian subgroup D_{2h}). Hence, instead of calculating the lowest d^8s^2 state directly, it may be more accurate to calculate higher d^8s^2 states and extrapolate the ground d^8s^2 (see Section B.6). The revised energies are given in Table B.4, rows 4-6.

Electron-correlation calculations were also performed on the Pt atom, on Q-Chem version 4.0 using the MP2 and CCSD methods on the LACVP basis set with ECP. A guess wavefunction with the correct orbital population was first generated by DFT methods, and then the electron-correlation values were calculated with the orbital overlap maximized. The results, given in Table B.5, are in decent agreement with the experimental values, but are not an improvement over DFT methods.

Table B.5. Excitation energies of Pt atom calculated using electron-correlation methods.

Config.	Exp.	MP2	CCSD
d^9s^1		-118.284	-118.289
d^{10}	11.07	13.41	16.83
d^8s^2	14.76	5.43	0.92
$\delta\delta$ (a)		30.16	12.41
$\pi\pi$ (b)		11.37	3.29
$\sigma\delta$ (c)	14.76	5.10	0.24

The d^9s^1 row contains the absolute energies in hartrees. The other rows contain the energies relative to the d^9s^1 ground state, in kcal/mol. Experimental energies derived from Moore [1]. Color coding represents deviation from experimental value. Blue: within 5 kcal/mol; green: within 10 kcal/mol; yellow: within 15 kcal/mol.

(a) Energy of the d^8s^2 configuration with singly occupied d_{xy} and $d_{x^2-y^2}$ orbitals.

(b) Energy of the d^8s^2 configuration with singly occupied d_{xz} and d_{yz} orbitals.

(c) Extrapolated energy of the ground d^8s^2 configuration according to the formula $E_{\sigma\delta} = \frac{4}{3}E_{\pi\pi} - \frac{1}{3}E_{\delta\delta}$.

Unfortunately, neither method gave the correct ordering of states; both methods put the singlet state at the highest energy. Furthermore, CCSD performed more poorly than MP2. This observation is probably due to the fact that CCSD is designed for calculating ground state energies.

We can draw several conclusions from the data presented for the Pt atom. First, DFT values are closer to the relativistic HF calculations than to the nonrelativistic calculations (see Table B.1). This is due to the effective core potential taking relativistic effects into account. Secondly, for the $d^9s^1 - d^{10}$ transition, most DFTs gave values that were a little high, while the HF calculation gave a value that was much too high. Thirdly, most DFTs ordered the relative energy levels of the different configurations in the same way as Martin and Hay's relativistic HF values, differently from the experimental result. And finally, M06-2X gave the best values.

B.3.2 Palladium (0)

Calculations with Pd were performed on Jaguar version 7.5 using the basis set LACV3P**++ [4], and on Q-Chem version 4.0 using the basis set LACVP [6]. The results from Jaguar are presented in Table B.6; however, it was difficult to calculate the d^8s^2 configuration properly due to the wide separation from d^9s^1 and the aforementioned symmetry issues. Hence, all DFT values were recalculated in Q-Chem; the results are presented in Table B.7. The $d^{10} - d^9s^1$ energy gap is very similar to the numbers in Jaguar; hence we can expect reasonably accurate values for the d^8s^2 configuration as well. In addition, the use of Q-Chem allows us to take advantage of the electron-correlation MP2 and CCSD methods.

It can be concluded from the tables for palladium that the best overall method was MP2, whereas

Table B.6. $d^{10} - d^9s^1$ Excitation energies of Pd atom as calculated by Jaguar.

Config.	Exp.	HF	B3LYP	M06	M06-2X	M06-HF	M06-L	PBE	PBE0
d^{10}		−125.87	−126.72	−126.72	−126.61	−126.52	−126.75	−126.68	−126.67
d^9s^1	21.91	1.97	20.79	38.15	27.53	10.89	28.16	22.28	20.72

The d^{10} row contains the absolute energies in hartrees. The d^9s^1 row contains the energies relative to the d^{10} ground state, in kcal/mol. Experimental energy derived from Moore [1]. Color coding represents deviation from experimental value. Gray: within 2 kcal/mol; blue: within 5 kcal/mol; green: within 10 kcal/mol; yellow: within 15 kcal/mol.

Table B.7. Excitation energies of Pd atom as calculated by Q-Chem.

Config.	Exp.	HF	MP2	CCSD	B3LYP	M06	M06-2X	M06-HF	M06-L	PBE	PBE0
d^{10}		−125.87	−125.97	−125.96	−126.71	−126.71	−126.61	−126.51	−126.74	−125.90	−126.67
d^9s^1	21.91	1.72	22.42	15.95	19.98	38.63	26.07	10.09	30.66	9.43	19.99
d^8s^2	77.94	55.17	80.54	67.28	84.79	114.45	97.61	89.50	97.18	67.17	88.40

The d^{10} row contains the absolute energies in hartrees. The other rows contain the energies relative to the d^{10} ground state, in kcal/mol. Experimental energy derived from Moore [1]. Color coding represents deviation from experimental value. Gray: within 2 kcal/mol; blue: within 5 kcal/mol; green: within 10 kcal/mol; yellow: within 15 kcal/mol.

the best DFT calculation was B3LYP.

B.3.3 Nickel (0)

Unlike the cases for Pt and Pd, calculations with Ni were performed without any effective core potential, using the basis set G3LARGE with the program Q-Chem version 4.0. The results are summarized in Table B.8 for the electron-correlation methods and Table B.9 for the DFT methods.

It can be concluded from the tables for nickel that the best overall method was CCSD, whereas

Table B.8. Excitation energies of Ni atom as calculated by Q-Chem; electron-correlation methods.

Config.	Exp.	HF	MP2	CCSD
d^8s^2		−1506.83	−1507.83	−1507.78
d^9s^1	−0.69*	1.72	−30.92	0.49
d^{10}	39.43	55.17	−44.60	47.07

The d^{10} row contains the absolute energies in hartrees. The other rows contain the energies relative to the d^{10} ground state, in kcal/mol. Experimental energy derived from Moore [1]. Color coding represents deviation from experimental value. Gray: within 2 kcal/mol; blue: within 5 kcal/mol; green: within 10 kcal/mol; red: within 25 kcal/mol.

* See the discussion for Table B.1.

Table B.9. Excitation energies of Ni atom as calculated by Q-Chem; DFT methods.

Config.	Exp.	XYGJ-OS	B3LYP	M06	M06-2X	M06-HF	M06-L	PBE	PBE0
d^8s^2		−1507.36	−1508.31	−1508.19	−1508.24	−1508.35	−1508.03	−1506.75	−1508.02
d^9s^1	−0.69*	−5.66	−9.11	−10.33	−3.59	−14.01	5.26	−12.30	−9.18
d^{10}	39.43	19.57	22.65	19.43	48.36	49.11	50.00	29.37	85.06

The d^{10} row contains the absolute energies in hartrees. The other rows contain the energies relative to the d^{10} ground state, in kcal/mol. Experimental energy derived from Moore [1]. Color coding represents deviation from experimental value. Blue: within 5 kcal/mol; green: within 10 kcal/mol; yellow: within 15 kcal/mol; red: within 25 kcal/mol.
* See the discussion for Table B.1.

Table B.10. Excitation energies of the group 10 atoms from d^9 to d^8s^1, as calculated using various DFTs.

	Exp.	XYGJ-OS	B3LYP	M06	M06-2X	M06-HF	M06-L	PBE	PBE0
Ni^+ d^9	175.03	390.57	173.62	166.76	167.85	156.59	75.48	164.53	167.67
d^8s^1	199.93	392.65	201.51	209.30	199.48	187.66	105.56	183.01	193.56
ΔE	24.90	2.08	27.89	42.54	31.63	31.07	30.08	18.48	25.90
Pd^+ d^9	197.30	N/A	198.16	209.32	196.01	182.01	196.53	177.85	193.77
d^8s^1	271.61	N/A	287.29	323.64	298.99	280.43	297.30	250.10	282.91
ΔE	74.31	N/A	89.14	114.33	102.98	98.42	100.77	72.25	89.14
Pt^+ d^9	195.09	N/A	217.38	207.69	206.89	212.36	203.26	208.54	211.33
d^8s^1	212.62	N/A	242.80	253.62	242.30	238.70	237.12	233.96	235.47
ΔE	17.53	N/A	25.42	45.92	35.41	26.34	33.86	25.42	24.14

All numbers are given in kcal/mol relative to d^8s^2 for Ni, d^{10} for Pd, and d^9s^1 for Pt. Experimental energy derived from Moore [1]. Color coding represents deviation from experimental value. Gray: within 2 kcal/mol; blue: within 5 kcal/mol; green: within 10 kcal/mol; yellow: within 15 kcal/mol; red: within 25 kcal/mol. XYGJ-OS not implemented for ECP; hence only Ni was calculated.

the best DFT calculation was M06-2X.

B.4 The singly-charged cation

Whereas the neutral group 10 metals each have different ground state configurations, the singly-charged cations Ni^+, Pd^+, and Pt^+ are uniformly d^9 in the ground state. The excitation energy from d^9 to d^8s^1 for each metal has been calculated by various DFTs and electron-correlation methods. A summary of the results, along with the experimental values [1], is given in tables B.10 and B.11. All calculations were done on Q-Chem version 4.0. The G3LARGE basis set was used for Ni^+ while the LACVP basis set with ECP was used for Pd^+ and Pt^+.

An examination of the data presented in tables B.10 and B.11 shows that CCSD is unequivocally the best method for Ni^+, while B3LYP is the best DFT method. M06-2X and PBE0 also gave good

Table B.11. Excitation energies of the group 10 atoms from d^9 to d^8s^1, as calculated using various electron-correlation methods.

	Exp.	HF	MP2	CCSD
Ni$^+$ d^9	175.03	252.85	140.27	167.93
d^8s^1	199.93	162.26	192.18	192.82
ΔE	24.90	-90.59	51.91	24.90
Pd$^+$ d^9	197.30	147.93	176.65	171.10
d^8s^1	271.61	217.87	283.37	251.33
ΔE	74.31	69.94	106.72	80.22
Pt$^+$ d^9	195.09	178.87	188.91	188.25
d^8s^1	212.62	188.39	205.44	205.81
ΔE	17.53	9.52	16.54	17.57

All numbers are given in kcal/mol relative to d^8s^2 for Ni, d^{10} for Pd, and d^9s^1 for Pt. Experimental energy derived from Moore [1]. Color coding represents deviation from experimental value. Gray: within 2 kcal/mol; blue: within 5 kcal/mol; green: within 10 kcal/mol; red: within 25 kcal/mol.

results. As for Pt$^+$, both CCSD and MP2 gave excellent results. Unfortunately, there was no single method for Pd$^+$ that gave good results for all energies: most methods were good at estimating the d^9 state; only M06-HF and PBE0 came close to estimating the d^8s^1 state; and HF, CCSD, and PBE were able to approximate the energy difference between the ion states well. Overall, however, these numbers are all nonetheless in better agreement with experimental data than the previous calculations as presented in Table B.2.

B.5 Angular momentum-dependent artifacts in DFT calculations

During the course of calculating these energies it became apparent that certain artifacts were being introduced in the calculations of the cations. These errors have been documented before [7] and the reason is innate to the nature of the exchange functional of DFT [8]. Potential solutions have been proposed [9] [10] but not yet widely implemented.

B.5.1 Angular momentum of the electron/hole in the d^1/d^9 configuration of the cation

The various microstates of a d^1 or d^9 configuration give rise to only one permissible spin state: ^2D. Hence, it should not matter which real d orbital contains the electron or hole, respectively. However, we find that for DFT methods the calculated energy does vary: For example, according to B3LYP the

Table B.12. “Degenerate” energies of the Pt$^+$ d^9 ground state.

d^9 hole	LACV3P**++		LACV3P		LAV1S	
	Energy	E_{rel}	Energy	E_{rel}	Energy	E_{rel}
z^2	−118.739	0.000	−118.738	0.000	−26.961	0.000
xy	−118.741	−1.123	−118.740	−1.157	−26.960	0.791
x^2-y^2	−118.741	−1.123	−118.740	−1.154	−26.960	0.870
xz	−118.737	1.141	−118.736	1.079	−26.958	1.591
yz	−118.737	1.141	−118.736	1.078	−26.958	1.591

Calculations done in Jaguar. The “Energy” columns contain values in hartrees, whereas the “E_{rel}” columns contain values in kcal/mol.

Table B.13. “Degenerate” energies of the Pt^{9+} d^1 ground state.

d^1	Energy	E_{rel}
z^2	−98.151343	0.000
xy	−98.151819	−0.299
x^2-y^2	−98.151822	−0.301
xz*	−98.151822	−0.301
yz*	−98.151822	−0.301

M06-2X/LACV3P**++ done in Jaguar. The “Energy” column contains values in hartrees, whereas the “E_{rel}” column contains values in kcal/mol.

* Jaguar could only run these calculations using Abelian (D_{2h}) symmetry. Therefore, when the electron was localized in a π symmetry orbital, the $d_{x^2-y^2}$ and d_{z^2} orbitals mixed and thus the d_{xz} or d_{yz} orbital was reanalyzed into a δ symmetry orbital. Hence the energy is not expected to differ from the energy of the d_{xy} or $d_{x^2-y^2}$ hole.

energy of the ion Pt$^+$ is different whether the hole is of σ symmetry (d_{z^2}, $L=0$), π symmetry (d_{xz} or d_{yz}, $L=1$), or δ symmetry ($d_{x^2-y^2}$ or d_{xy}, $L=2$). The specific numbers are given in Table B.12. Similarly, the energy of Pt^{9+} as calculated by M06-2X depends (completely unphysically) on which orbital the lone d electron is placed (Table B.13).

A more extensive study was done on the Ni$^+$ ion, using Q-Chem version 4.0. The results of calculations using DFT methods are given in Table B.14 and the results of calculations using electron-correlation methods are given in Table B.15. It is clear that, whereas the electron-correlation methods correctly predict the degeneracy of the five d holes in ^2D Ni$^+$, the DFT methods mostly do not. The only exception among the DFTs is XYGJ-OS, a double-hybrid DFT.

Table B.14. “Degenerate” energies of the Ni$^+$ d^9 ground state as calculated by DFT methods.

d^9	B3LYP	M06	M06-2X	M06-HF	M06-L	PBE	PBE0	XYGJ-OS
z^2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
xy	0.293	0.407	−0.589	−1.681	−0.285	−0.111	0.372	0.000
$x^2 - y^2$	0.289	0.414	−0.560	−1.603	−0.329	−0.109	0.369	−0.001
xz*	0.290	0.416	−0.583	−1.675	−0.276	−0.111	0.358	0.018
yz*	0.290	0.430	−0.568	−1.647	−0.287	−0.109	0.359	0.016

Energies are relative to the d_{z^2} hole and in kcal/mol.
* Because Q-Chem runs the calculations using Abelian (D_{2h}) symmetry, when the electron was localized in a π symmetry orbital, the $d_{x^2-y^2}$ and d_{z^2} orbitals mixed and thus the d_{xz} or d_{yz} orbital was reanalyzed into a δ symmetry orbital. Hence the energy is not expected to differ from the energy of the d_{xy} or $d_{x^2-y^2}$ hole.

Table B.15. Degenerate energies of the Ni$^+$ d^9 ground state as calculated by electron-correlation methods.

d^9	HF	MP2	CCSD
z^2	0.000	0.000	0.000
xy	−0.012	0.007	−0.002
$x^2 - y^2$	−0.008	0.007	−0.002
xz*	0.000	0.023	−0.002
yz*	−0.001	0.009	−0.002

Energies are relative to the d_{z^2} hole and in kcal/mol.
* Because Q-Chem runs the calculations using Abelian (D_{2h}) symmetry, when the electron was localized in a π symmetry orbital, the $d_{x^2-y^2}$ and d_{z^2} orbitals mixed and thus the d_{xz} or d_{yz} orbital was reanalyzed into a δ symmetry orbital. Hence the energy is not expected to differ from the energy of the d_{xy} or $d_{x^2-y^2}$ hole.

Table B.16. Energies of the Pt^{2+} d^8 configuration, calculated by B3LYP/LACV3P**++.

Hole type		Energy	E_{rel}
z^2, x^2-y^2	$\sigma\delta$	−118.0461	0.00
xy, z^2	$\sigma\delta$	−118.0461	0.02
xz, yz	$\pi\pi$	−118.0372	5.59
xz, x^2-y^2	$\pi\delta$	−118.0366	6.00
yz, x^2-y^2	$\pi\delta$	−118.0366	6.00
xz, xy	$\pi\delta$	−118.0359	6.43
yz, xy	$\pi\delta$	−118.0359	6.43
xz, z^2	$\sigma\pi$	−118.0201	16.33
yz, z^2	$\sigma\pi$	−118.0201	16.33
xy, x^2-y^2	$\delta\delta$	−118.0145	19.84

Energies are in hartrees; E_{rel} values are in kcal/mol.

B.5.2 Angular momentum of the holes in the d^8 configuration of the dication

When there are two holes, there are two triplet states: ${}^3F$ and ${}^3P$. In terms of the real orbital holes, there are several intermediate energy levels: the $\sigma\delta$ holes are at ${}^3F$; the $\pi\pi$ and $\pi\delta$ holes are at $\frac{4}{5}{}^3F + \frac{1}{5}{}^3P$, the $\sigma\pi$ holes are at $\frac{2}{5}{}^3F + \frac{3}{5}{}^3P$, and the $\delta\delta$ holes are at $\frac{1}{5}{}^3F + \frac{4}{5}{}^3P$. These values are derived in the Section B.6.

Table B.16 has the values for Pt^{2+} calculated in B3LYP with the LACV3P**++ basis set in Jaguar. While the numbers are close to the theoretically predicted values, the $\pi\pi$ and $\pi\delta$ holes are split into three different sets of closely spaced energy levels. As in the case of the d^9 M^+ ions, this is an artifact of the DFT calculation and is not physical.

Similar calculations were also performed for Pd^{2+}. The results are shown in Table B.17. However, due to difficulties with Jaguar, Q-Chem was used instead. The reduction of the atom to an Abelian subgroup prevented the calculation of $\pi\delta$ and $\sigma\pi$ holes, however. Fortunately, the calculated $\sigma\delta$, $\pi\pi$, and $\delta\delta$ holes are in good agreement with experiment.

The most extensive calculations were done on nickel. Values calculated with Jaguar are given in Table B.18 while values calculated with Q-Chem and experimental values are given in Table B.19. Again, note that it was not possible to get $\pi\delta$ and $\sigma\pi$ hole energies with Q-Chem.

B.6 Energies of d^2 and d^8 triplet states

Given a d^2 or d^8 atomic configuration, we can easily derive that the various microstates give rise to the ${}^3F$ and ${}^3P$ triplet states and the ${}^1G$, ${}^1D$, and ${}^1S$ singlet states. Furthermore, we know from

Table B.17. Energies of the Pd^{2+} d^8 configuration, calculated by B3LYP/LACVP.

Hole type		Energy	E_{rel}	Exp/J (a)	Exp/avg (b)
z^2, x^2-y^2	$\sigma\delta$	-125.663	0.00	0.00	0.00
xy, z^2	$\sigma\delta$	-125.663	0.01	0.00	0.00
xz, yz	$\pi\pi$	-125.651	7.45	7.83	6.46
xz, x^2-y^2	$\pi\delta$	-125.663	0.01 (c)	7.83	6.46
yz, x^2-y^2	$\pi\delta$	-125.663	0.01 (c)	7.83	6.46
xz, xy	$\pi\delta$	-125.651	7.45 (d)	7.83	6.46
yz, xy	$\pi\delta$	-125.651	7.45 (d)	7.83	6.46
xz, z^2	$\sigma\pi$	-125.663	0.01 (c)	23.50	19.38
yz, z^2	$\sigma\pi$	-125.663	0.01 (c)	23.50	19.38
xy, x^2-y^2	$\delta\delta$	-125.619	27.93	31.33	25.84

Energies are in hartrees; E_{rel} and experimental values are in kcal/mol. Experimental values from [1].
(a) Experimental value using the lowest J energy.
(b) Experimental value derived from the average of spin-orbit coupling.
(c) Collapsed to $\sigma\delta$.
(d) Collapsed to $\pi\pi$.

Table B.18. Energies of the Ni^{2+} d^8 configuration, calculated on Jaguar using the 6-31G(tm)**++ basis.

Hole type		HF	B3LYP	M06	M06-2X	M06-HF	M06-L	PBE	PBE0
z^2, x^2-y^2	$\sigma\delta$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
xy, z^2	$\sigma\delta$	0.00	0.05	-0.27	-0.83	-0.53	-0.42	0.08	0.06
xz, yz	$\pi\pi$	11.29	10.25	10.35	4.13	-7.93	16.22	10.23	10.37
xz, x^2-y^2	$\pi\delta$	11.62	9.80	7.50	6.05	0.52	13.17	9.39	9.79
yz, x^2-y^2	$\pi\delta$	11.62	9.80	7.50	6.05	0.52	13.17	9.39	9.79
xz, xy	$\pi\delta$	11.62	10.42	10.49	4.29	-7.70	16.38	10.38	10.53
yz, xy	$\pi\delta$	11.62	10.42	10.49	4.29	-7.70	16.38	10.38	10.53
xz, z^2	$\sigma\pi$	34.34	28.33	18.12	19.90	10.28	35.85	26.60	28.15
yz, z^2	$\sigma\pi$	34.34	28.33	18.12	19.90	10.28	35.85	26.60	28.15
xy, x^2-y^2	$\delta\delta$	45.42	38.44	23.84	26.92	14.84	48.36	36.66	38.33

Energies are in kcal/mol.
(a) Experimental value using the lowest J energy.
(b) Experimental value derived from the average of spin-orbit coupling.
(c) Collapsed to $\sigma\delta$.
(d) Collapsed to $\pi\pi$.

Table B.19. Energies of the Ni^{2+} d^8 configuration, experimental and calculated on Q-Chem using the G3LARGE basis.

Hole type		Exp/J (a)	Exp/avg (b)	XYGJ-OS	MP2	CCSD
z^2, x^2-y^2	$\sigma\delta$	0.00	0.00	0.00	0.00	0.00
xy, z^2	$\sigma\delta$	0.00	0.00	−0.03	0.00	0.00
xz, yz	$\pi\pi$	9.53	9.00	9.39	8.54	7.58
xz, x^2-y^2	$\pi\delta$	9.53	9.00	0.00 (c)	−0.01 (c)	0.00 (c)
yz, x^2-y^2	$\pi\delta$	9.53	9.00	0.00 (c)	0.00 (c)	0.00 (c)
xz, xy	$\pi\delta$	9.53	9.00	9.39 (d)	8.54 (d)	7.58 (d)
yz, xy	$\pi\delta$	9.53	9.00	9.39 (d)	8.54 (d)	7.58 (d)
xz, z^2	$\sigma\pi$	28.58	27.01	0.00 (c)	35.08 (e)	35.09 (e)
yz, z^2	$\sigma\pi$	28.58	27.01	0.00 (c)	0.00 (c)	0.00 (c)
xy, x^2-y^2	$\delta\delta$	38.11	36.02	37.82	35.08	35.09

Energies are in kcal/mol.
(a) Experimental value using the lowest J energy.
(b) Experimental value derived from the average of spin-orbit coupling.
(c) Collapsed to $\sigma\delta$.
(d) Collapsed to $\pi\pi$.
(e) Collapsed to $\delta\delta$.

Hund's rules that the ^3F state is the ground state. However, sometimes it is useful to know the energy given the two electrons or holes in specific, real orbitals (e.g., d_{z^2} or d_{xy}). In this case we must calculate the energies of intermediate states, i.e. between that of ^3F and ^3P.

B.6.1 Background

The d orbital electrons, which have $\ell = 2$, can be represented by either the complex spherical harmonics Y_{2m} or the real spherical harmonics Z_{2m}. Below is a list of the complex spherical harmonics:

$$
\begin{aligned}
r^2 Y_{2\bar{2}} &= \sqrt{\frac{15}{32\pi}}(x-iy)^2 \\
r^2 Y_{2\bar{1}} &= \sqrt{\frac{15}{8\pi}}z(x-iy) \\
r^2 Y_{20} &= \sqrt{\frac{5}{16\pi}}(2z^2-x^2-y^2) \\
r^2 Y_{21} &= \sqrt{\frac{15}{8\pi}}z(x+iy) \\
r^2 Y_{22} &= \sqrt{\frac{15}{32\pi}}(x+iy)^2
\end{aligned}
$$

And of the real spherical harmonics:

$$r^2 Z_{2\bar{2}} = \sqrt{\frac{15}{4\pi}} xy$$
$$r^2 Z_{2\bar{1}} = \sqrt{\frac{15}{4\pi}} yz$$
$$r^2 Z_{20} = \sqrt{\frac{5}{16\pi}} (2z^2 - x^2 - y^2)$$
$$r^2 Z_{21} = \sqrt{\frac{15}{4\pi}} xz$$
$$r^2 Z_{22} = \sqrt{\frac{15}{16\pi}} (x^2 - y^2)$$

It is easy to see that the complex and the real spherical harmonics are closely related:

$$Y_{2\bar{2}} = \frac{1}{\sqrt{2}}(Z_{22} - iZ_{2\bar{2}})$$
$$Y_{2\bar{1}} = \frac{1}{\sqrt{2}}(Z_{21} - iZ_{2\bar{1}})$$
$$Y_{21} = \frac{1}{\sqrt{2}}(Z_{21} + iZ_{2\bar{1}})$$
$$Y_{22} = \frac{1}{\sqrt{2}}(Z_{22} + iZ_{2\bar{2}})$$

$$Y_{20} = Z_{20}$$

$$Z_{2\bar{2}} = \frac{1}{\sqrt{2}i}(Y_{22} - Y_{2\bar{2}})$$
$$Z_{2\bar{1}} = \frac{1}{\sqrt{2}i}(Y_{21} - Y_{2\bar{1}})$$
$$Z_{21} = \frac{1}{\sqrt{2}}(Y_{21} + Y_{2\bar{1}})$$
$$Z_{22} = \frac{1}{\sqrt{2}}(Y_{22} + Y_{2\bar{2}})$$

B.6.2 The d^2 and d^8 triplet states

The triplet states are ${}^3F$ and ${}^3P$. We shall now examine the complex spherical harmonic wavefunctions associated with the M_L values of each state. To do so we will start with the highest possible M_L value and successively apply the lowering operator $\hat{L}_-$:

$$\hat{L}_- |\ell m\rangle = \sqrt{(\ell + m)(\ell - m + 1)} |\ell m - 1\rangle.$$

Also, we will use $\mathcal{A}$ to represent antisymmetric functions, e.g., $\mathcal{A}[UV] = UV - VU$.

B.6.2.1 The ^3F state

The ^3F state has M_L values that range from -3 to 3. For $M_L = 3$ the only possible configuration is $\mathcal{A}[Y_{22}Y_{21}]$. Similarly, for $M_L = 2$ the only possible configuration is $\mathcal{A}[Y_{22}Y_{20}]$.

For $M_L = 1$, however, we note that $\hat{L}_-$ can act on either Y_{22} or Y_{20}; consequently we get a mix:

$$\mathcal{A}[2Y_{21}Y_{20} + \sqrt{6}Y_{22}Y_{2\bar{1}}];$$

which is normalized to

$$\mathcal{A}[\sqrt{\frac{2}{5}}Y_{21}Y_{20} + \sqrt{\frac{3}{5}}Y_{22}Y_{2\bar{1}}].$$

For $M_L = 0$, applying $\hat{L}_-$ once again yields

$$\mathcal{A}[\sqrt{\frac{2}{5}}(\sqrt{6}Y_{21}Y_{2\bar{1}}) + \sqrt{\frac{3}{5}}(2Y_{21}Y_{2\bar{1}} + 2Y_{22}Y_{2\bar{2}})],$$

which simplifies and normalizes to

$$\mathcal{A}[\frac{2}{\sqrt{5}}Y_{21}Y_{2\bar{1}} + \frac{1}{\sqrt{5}}Y_{22}Y_{2\bar{2}}].$$

By symmetry arguments we can see that $M_L = -1$ corresponds to

$$\mathcal{A}[\sqrt{\frac{2}{5}}Y_{20}Y_{2\bar{1}} + \sqrt{\frac{3}{5}}Y_{21}Y_{2\bar{2}}];$$

We also see that $M_L = -2$ corresponds to $\mathcal{A}[Y_{20}Y_{2\bar{2}}]$ and $M_L = -3$ corresponds to $\mathcal{A}[Y_{2\bar{2}}Y_{2\bar{2}}]$.

B.6.2.2 The ^3P state

The ^3P state has M_L values that range from -1 to 1. For $M_L = 1$ the wavefunction must be orthogonal to the ^3F $M_L = 1$ case; it is easy to see that the wavefunction

$$\mathcal{A}[\sqrt{\frac{3}{5}}Y_{21}Y_{20} - \sqrt{\frac{2}{5}}Y_{22}Y_{2\bar{1}}]$$

fulfills this condition. Likewise, for $M_L = 0$ it is easy to see that

$$\mathcal{A}[\frac{1}{\sqrt{5}}Y_{21}Y_{2\bar{1}} - \frac{2}{\sqrt{5}}Y_{22}Y_{2\bar{2}}]$$

is orthogonal to the ^3F $M_L = 0$ configuration.

By symmetry we can add that

$$\mathcal{A}[\sqrt{\frac{3}{5}}Y_{20}Y_{2\bar{1}} - \sqrt{\frac{2}{5}}Y_{21}Y_{2\bar{2}}]$$

corresponds to the ^3P $M_L = -1$ case.

B.6.3 Pure and mixed complex orbital configurations

In the previous section, we saw that the complex orbital configurations $\mathcal{A}[Y_{22}Y_{21}]$, $\mathcal{A}[Y_{22}Y_{20}]$, $\mathcal{A}[Y_{20}Y_{2\bar{2}}]$, and $\mathcal{A}[Y_{2\bar{1}}Y_{2\bar{2}}]$ are pure ^3F states, while the other combinations are mixed. In this section we shall deconvolute the mixed states.

B.6.3.1 $M_L = 1$

We have

$$\Psi_1^{^3F} = \mathcal{A}[\sqrt{\frac{2}{5}}Y_{21}Y_{20} + \sqrt{\frac{3}{5}}Y_{22}Y_{2\bar{1}}]$$

and

$$\Psi_1^{^3P} = \mathcal{A}[\sqrt{\frac{3}{5}}Y_{21}Y_{20} - \sqrt{\frac{2}{5}}Y_{22}Y_{2\bar{1}}];$$

Hence

$$\mathcal{A}[Y_{21}Y_{20}] = \sqrt{\frac{2}{5}}\Psi_1^{^3F} + \sqrt{\frac{3}{5}}\Psi_1^{^3P}$$

and

$$\mathcal{A}[Y_{22}Y_{2\bar{1}}] = \sqrt{\frac{3}{5}}\Psi_1^{^3F} - \sqrt{\frac{2}{5}}\Psi_1^{^3P}.$$

B.6.3.2 $M_L = 0$

We have

$$\Psi_0^{^3F} = \mathcal{A}[\frac{2}{\sqrt{5}}Y_{21}Y_{2\bar{1}} + \frac{1}{\sqrt{5}}Y_{22}Y_{2\bar{2}}]$$

and

$$\Psi_0^{^3P} = \mathcal{A}[\frac{1}{\sqrt{5}}Y_{21}Y_{2\bar{1}} - \frac{2}{\sqrt{5}}Y_{22}Y_{2\bar{2}}];$$

Hence

$$\mathcal{A}[Y_{21}Y_{2\bar{1}}] = \frac{2}{\sqrt{5}}\Psi_0^{^3F} + \frac{1}{\sqrt{5}}\Psi_0^{^3P}$$

and

$$\mathcal{A}[Y_{22}Y_{2\bar{2}}] = \frac{1}{\sqrt{5}}\Psi_0^{^3F} - \frac{2}{\sqrt{5}}\Psi_0^{^3P}.$$

B.6.3.3 $M_L = -1$

From symmetry with the $M_L = 1$ case we have

$$\mathcal{A}[Y_{20}Y_{2\bar{1}}] = \sqrt{\frac{2}{5}}\Psi_{-1}^{^3F} + \sqrt{\frac{3}{5}}\Psi_{-1}^{^3P}$$

and

$$\mathcal{A}[Y_{21}Y_{2\bar{2}}] = \sqrt{\frac{3}{5}}\Psi_{-1}^{^3F} - \sqrt{\frac{2}{5}}\Psi_{-1}^{^3P}.$$

B.6.4 Real orbital configuration energies

We are now ready to calculate the energies of the configuration of electrons or holes in real orbitals. We should first note that the d_{z^2} orbital (Z_{20}) has σ symmetry, the d_{xz} and d_{yz} orbitals (Z_{21} and $Z_{2\bar{1}}$) have π symmetry, and the $d_{x^2-y^2}$ and d_{xy} orbitals (Z_{22} and $Z_{2\bar{2}}$) have δ symmetry. Also, let us define $\epsilon = E(^3P) - E(^3F)$ as the excitation energy to ^3P.

B.6.4.1 Energy of $\sigma\pi$ and $\sigma\overline{\pi}$

$$\sigma\pi \equiv \mathcal{A}[Z_{21}Z_{20}] = \mathcal{A}[\frac{Y_{20}}{\sqrt{2}}(Y_{21} + Y_{2\bar{1}})]$$

$$\begin{aligned} E(Z_{21}Z_{20}) &= \frac{1}{2}(E(Y_{21}Y_{20}) + E(Y_{2\bar{1}}Y_{20})) \\ &= \frac{1}{2}[(\frac{2}{5}E(^3F) + \frac{3}{5}E(^3P)) + (\frac{2}{5}E(^3F) + \frac{3}{5}E(^3P))] \\ &= \frac{2}{5}E(^3F) + \frac{3}{5}E(^3P) = E(^3F) + \frac{3}{5}\epsilon \end{aligned}$$

A very similar calculation for the $\sigma\overline{\pi}$ case yields the same energy, $\frac{3}{5}\epsilon$ above the ground state.

B.6.4.2 Energy of $\sigma\delta$ and $\sigma\overline{\delta}$

$$\sigma\delta \equiv \mathcal{A}[Z_{22}Z_{20}] = \mathcal{A}[\frac{Y_{20}}{\sqrt{2}}(Y_{22} + Y_{2\bar{2}})]$$

$$E(Z_{22}Z_{20}) = \frac{1}{2}(E(Y_{22}Y_{20}) + E(Y_{2\bar{2}}Y_{20})) = \frac{1}{2}[E(^3F) + E(^3F)] = E(^3F)$$

A very similar calculation for the $\sigma\overline{\delta}$ case yields the same energy, i.e. the energy of the ground state.

B.6.4.3 Energy of $\pi\overline{\pi}$

$$\pi\overline{\pi} \equiv \mathcal{A}[Z_{21}Z_{2\bar{1}}] = \mathcal{A}[\frac{1}{2i}(Y_{21} + Y_{2\bar{1}})(Y_{21} - Y_{2\bar{1}})] = \frac{1}{\sqrt{2}i}(Y_{21}Y_{2\bar{1}} - Y_{2\bar{1}}Y_{21})$$

$$E(Z_{21}Z_{2\bar{1}}) = \frac{1}{2}(E(Y_{21}Y_{2\bar{1}}) + E(Y_{2\bar{1}}Y_{21})) = E(Y_{21}Y_{2\bar{1}}) = \frac{4}{5}E(^3F) + \frac{1}{5}E(^3P) = E(^3F) + \frac{1}{5}\epsilon$$

B.6.4.4 Energy of $\pi\delta$, $\pi\overline{\delta}$, $\overline{\pi}\delta$, and $\overline{\pi}\overline{\delta}$

$$\pi\delta \equiv \mathcal{A}[Z_{22}Z_{21}] = \mathcal{A}[\frac{1}{2}(Y_{22}+Y_{2\bar{2}})(Y_{21}+Y_{2\bar{1}})] = \mathcal{A}[\frac{1}{2}(Y_{22}Y_{21}+Y_{22}Y_{2\bar{1}}+Y_{2\bar{2}}Y_{21}+Y_{2\bar{2}}Y_{2\bar{1}})]$$

$$\begin{aligned}E(Z_{22}Z_{21}) &= \frac{1}{4}[E(Y_{22}Y_{21})+E(Y_{22}Y_{2\bar{1}})+E(Y_{2\bar{2}}Y_{21})+E(Y_{2\bar{2}}Y_{2\bar{1}})]\\ &= \frac{1}{4}[E(^3F)+(\frac{3}{5}E(^3F)+\frac{2}{5}E(^3P))+(\frac{3}{5}E(^3F)+\frac{2}{5}E(^3P))+E(^3F)]\\ &= \frac{4}{5}E(^3F)+\frac{1}{5}E(^3P) = E(^3F)+\frac{1}{5}\epsilon\end{aligned}$$

Very similar calculations for the $\pi\overline{\delta}$, $\overline{\pi}\delta$, and $\overline{\pi}\overline{\delta}$ cases yield the same energy, i.e. $\frac{1}{5}\epsilon$ above the ground state.

B.6.4.5 Energy of $\delta\overline{\delta}$

$$\delta\overline{\delta} \equiv \mathcal{A}[Z_{22}Z_{2\bar{2}}] = \mathcal{A}[\frac{1}{2i}(Y_{22}+Y_{2\bar{2}})(Y_{22}-Y_{2\bar{2}})] = \frac{1}{\sqrt{2}i}(Y_{22}Y_{2\bar{2}}-Y_{2\bar{2}}Y_{22})$$

$$E(Z_{22}Z_{2\bar{2}}) = \frac{1}{2}(E(Y_{22}Y_{2\bar{2}})+E(Y_{2\bar{2}}Y_{22})) = E(Y_{22}Y_{2\bar{2}}) = \frac{1}{5}E(^3F)+\frac{4}{5}E(^3P) = E(^3F)+\frac{4}{5}\epsilon$$

B.6.5 Summary

A triplet d^2 or d^8 atomic configuration gives rise to a mix of ^3F and ^3P states. The $\sigma\delta$ configurations are pure ^3F, the $\pi\pi$ and $\pi\delta$ configurations are one-fifth of the way towards ^3P, the $\sigma\pi$ configurations are three-fifths of the way towards ^3P, and the $\delta\delta$ configuration is four-fifths of the way towards the ^3P energy level. Hence we see that the energy is the lowest when the electrons or holes are allowed to freely roam about the atom (the $\sigma\delta$ case) and the highest when they are restricted to one plane (the $\delta\delta$ case).

B.7 Conclusions

For the neutral atoms, M06-2X gave the best DFT results for Pt and Ni, while B3LYP gave the best DFT results for Pd. This may be due to the contraction of the d functions of the basis set in Pd. Considering only electron-correlation methods, MP2 gave the best results for Pt and Pd, while CCSD gave the best results for Ni. This may be due to the use of an ECP on Pt and Pd. In comparing DFT versus electron-correlation methods, the electron-correlation method (CCSD or MP2) was better for Pd and Ni, whereas the DFT M06-2X was better than any electron-correlation method for Pt. For the singly-charged cation, B3LYP gave the best results for Pt and Ni whereas there was no method found that gave good results for Pd.

The singly-charged cation in the d^9 configuration should have a hole in one of five degenerate orbitals; this is not borne out by DFT calculations and the discrepancy is not physical. The use of electron-correlation calculations removes this artifact. Similar issues are observed with the doubly-charged cation in the d^8 configuration. This problem is innate to DFT and its resolution is still an active area of research.

B.8 References

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