Finding Appropriate Methods to Calculate Metal and Metal Hydride XPS Spectra

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Introduction

The goal of this project is to evaluate methods to calculate metal and metal hydride XPS spectra from molecular structures. This will make it possible to calculate expected XPS spectra, and thus obtain information on the energy of electrons in the compound. Thus far, I have calculated core electron energy shifts between Copper and Nickel atoms and their hydrides, and between Copper Hydride and Copper Hydride complexes with ligands. We report correlations between core electron ionization energy shifts in Copper and Nickel complexes and other factors, such as the ligand used in the complex and partial charges on all atoms. We also report correlations between NMR chemical shifts and partial charges on all atoms. This will be used in the future to establish accurate and efficient methods for calculating transition metal XPS spectra.

Methods

- Copper
  - Model used: cc-pVDZ basis set, density-functional: Perdew 1986 correlation, PBE exchange.
  - Ligands used: ammonia, H_2, methylamine, dimethylamine, trimethylamine, CO, silanol, acetonitrile, methylisocyanide, hydroxymethyl carbene, methoxy carbene.
  - Calculated ground state and core ionized energies for Cu, HCu, HCu(ligand) compounds, which were used to calculate the core ionization energy (IE) for each orbital in each compound.
    - (Core Ionized Energy – Ground State Energy) = Core IE
    - Results are not as accurate as those that Chong obtained, because a lower level of theory was used [6].
  - Found the IE shift: difference in each orbital between HCu and each HCu(ligand) complex.
  - Found each IE shift with relativistic corrections, using constants from Chong's 2005 article [5].
    - $((2.198*10^{-7}) * IE^{2.178})$ = relativistic correction
    - These corrections are all less than .01 eV (and therefore negligible).
  - Graphing the core IE shifts against the sum $\Sigma(q_i/r_{ij})$ (where q_i is an atom's NPA charge and r_{ij} is its radius from the metal) for each compound gave a linear correlation with slope m.
    - Graphing (core IE shift) – $m\Sigma(q_i/r_{ij})$ against the NPA charge on Copper produces a very strong linear correlation with slope k for sigma donor ligands.
    - The formula, $Shift_M = kq_M + m\Sigma(q_j/r_{Mj}) + b$, is based on a formula from Siegbahn's book [8].
  - NMR chemical shifts for the HCu(ligand) complexes were calculated, using NWChem.
    - Graphing the NMR chemical shifts of the hydride H on each compound against the equation $kq_H + m\Sigma(q_i/r_{ij}) + b$ (where q_H is the partial charge on the hydride H, q_i is an atom's partial charge, r_{ij} is the atom's radius from the hydride, and m, k and b are optimized constants) for each compound gave a roughly linear correlation.
      - The constants m, k and b were optimized by minimizing the total of the differences between the NMR chemical shift and the equation $kq_H + m\Sigma(q_i/r_{ij}) + b$.
- Nickel
  - In order to find the best density functional to run the H_2Ni(ligand) calculations, Ni core IEs with cc-pVQZ basis set and 82 different density-functionals were calculated.
    - Density-functional effects are very nearly additive, so calculations for 15 combinations (exchange + correlation) and 18 hybrids were used to calculate the remaining combinations.
    - Analyzing the percent error of each density-functional shows that the density-functionals highlighted in yellow are the most accurate overall.
    - Comparing the percent errors of the density-functionals from experimental values, the BOP hybrid was determined to be the most accurate to calculate Ni core IE shifts.
  - Calculated ground state and core ionized energies for Ni, H_2Ni, H_2Ni(ligand) compounds (using the same ligands as for Copper) which were used to calculate the core IE and core IE shift for each orbital in each compound.
    - Model used: cc-pVDZ basis set, BOP hybrid density-functional.
  - Using the same method as for copper, the core IE shift was fit to the equation $Shift_M = kq_M + m\Sigma(q_j/r_{Mj}) + b$, and found to produce a strong correlation across all orbitals for compounds with one and two sigma donor ligands.

Future Study

- Find correlations between molecular properties for other types of ligands.
- Analyze connections between NMR chemical shifts and XPS shifts.
- Use both NMR and XPS data to test our methodology.
- Test uncontracted Pople style basis sets to determine accuracy and correlations.

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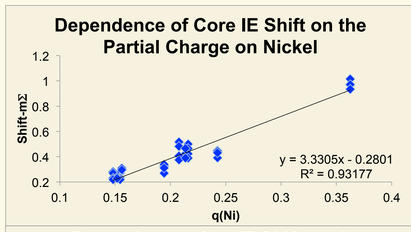
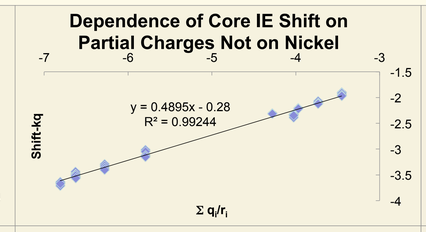
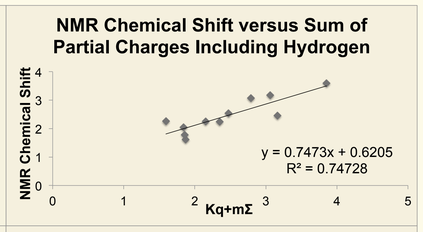
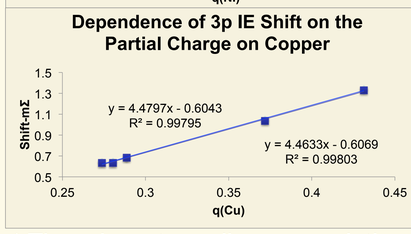
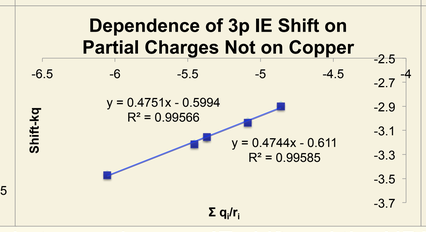
Results and Discussion

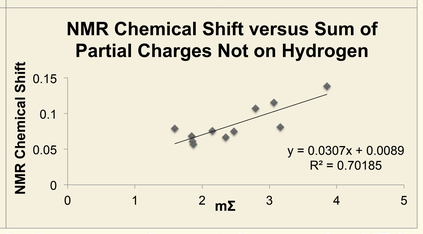




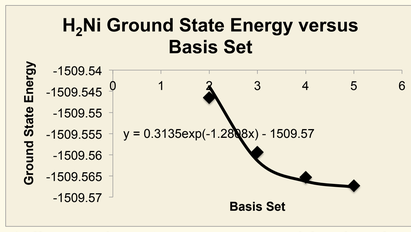


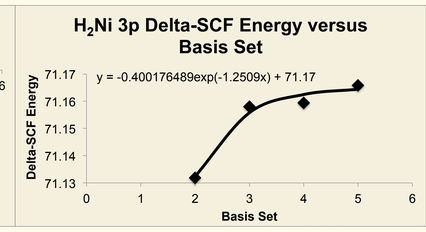


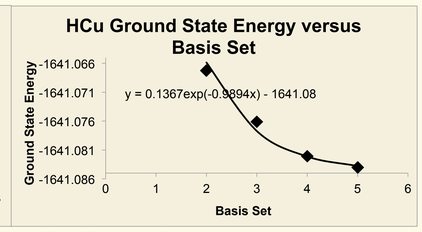




- There is a strong linear correlation between the core IE shift and the NPA charge on the metal, once the NPA charges on all other atoms are factored out of the shift.
- There is also a very strong linear correlation between the core IE shift and the sum of all NPA charges not on the metal, after the effect of the NPA charge on the metal is factored out of the shift.
- NMR chemical shifts are correlated strongly with the sum of all partial charges on the complex.
- This correlation becomes slightly weaker when the partial charge on the hydrogen itself is not considered.
- This correlation seems strongest for pi acceptor ligands, and weaker for sigma donor ligands.







- Ground state energy and ionization energy converge slowly with increasing basis set size.
- The difference in ionization energies is small.
- The cc-pVDZ through cc-pV5Z calculations form a exponential decay function, converging to -1641.08eV for the HCu ground state energy, -1509.57eV for the H_2Ni ground state energy, and 71.17eV for the H_2Ni 3p IE.

Density-Functional combinations: sum of % error of all orbitals

	Slater-Dirac	Becke86	PW86	Becke88	Gill96	Becke (EDF1)	Perdew91	PBE
vokso-wilk-nusair	32.30	29.08	31.76	34.38	35.27	28.85	29.46	29.14
perdew-zunger	38.37	36.13	86.82	89.44	90.33	36.90	36.06	36.26
wigner	42.00	39.32	90.45	93.07	93.97	40.10	39.26	39.45
perdew-wang 92	40.57	40.36	40.42	43.03	43.99	40.14	40.74	40.43
lee-yang-parr	75.18	78.82	34.77	33.11	32.58	78.08	79.08	78.73
perdew86	28.92	28.71	32.43	35.05	36.01	28.48	29.08	28.77
LYP refit	65.89	67.01	22.81	21.27	20.80	66.36	67.27	66.96
PW91	29.77	29.56	33.83	36.45	37.41	29.34	29.94	29.63

Hybrid % error of all orbitals

	B3PW91	BR89/B94	BR89/PK06	M06-L	M05	BOP	BECKE97-1	PBE96	EDF1	EDF2
2s	2.63	1.71	2.17	1.50	2.37	3.09	2.58	2.53	3.05	2.65
2p3	-0.42	-1.47	-0.76	-1.38	-0.39	-0.34	-0.41	-0.39	-0.39	-0.52
2p4	-0.37	-1.47	-0.76	-1.35	-0.39	-0.27	-0.41	-0.39	-0.31	-0.52
2p5	-0.37	-1.47	-0.76	-1.35	-0.31	-0.27	-0.36	-0.34	-0.31	-0.47
3s	0.12	-5.02	-1.58	-6.20	-0.87	2.08	0.06	-0.32	1.80	0.43
3p7	-8.47	-16.86	-9.84	-16.33	-9.24	-7.57	-8.68	-8.79	-7.79	-8.64
3p8	-8.37	-17.05	-9.84	-16.32	-9.14	-6.56	-8.68	-8.79	-6.90	-8.64
3p9	-8.37	-17.05	-10.05	-16.31	-9.14	-6.56	-8.29	-8.60	-6.90	-8.13
sum ea. shell	11.64	25.07	14.35	25.41	12.88	13.09	11.73	12.03	13.02	12.25
sum all orbitals	29.11	62.12	35.76	60.74	31.85	26.75	29.46	30.15	27.42	30.02

Conclusions

- By calculating the percent differences between calculated IE values for nickel atom and experimental values, the BOP hybrid density-functional was determined to be the most accurate for our nickel calculations.
- There are strong correlations between core IE shifts in Copper and Nickel complexes and the metal's NPA charge, after accounting for the other atoms' charges.
- There are strong correlations between NMR chemical shifts in Copper complexes and the partial charges, following an equation similar to that of ionization energy.