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 accurately and efficiently calculate expected XPS spectra, and thus obtain information on the energy of electrons in the compound. Thus far, I have calculated core electron ionization energy shifts between Copper and Nickel atoms and their hydrides, and between Copper Hydride and Copper Hydride complexes with ligands. This was done using QChem software with WebMO to run Density Functional and Ab-Initio calculations on the optimized molecular geometries. Currently, I am working to determine correlations between core electron ionization energy shifts in Copper and/or Nickel complexes and other factors, such as the ligands used in the complex or other physical properties of the molecule.

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
  - ❖Found the IE shift: difference in each orbital between HCu and each HCu(ligand) complex.
  - ❖Found each IE shift with relativistic corrections, using the constants from Chong's 2002 article [3]. My results are not as accurate as those that Chong obtained, because I was working at a lower level of theory.
    - ❖$((2.198*10^{-7}) * IE^{2.178})$ = relativistic modifier
    - ❖This modifier is added to the non-relativistic IE to obtain the relativistic IE.
  - ❖Graphed the IE shifts from each complex against their C1 values, percent ionicity, NPA charges on copper, partial charge, and dipole moment. This produced no linear correlations, but did produce two notable parabolic correlations.
  - ❖Repeated the process of finding the IE shifts for each complex using a Chemsol solvent model, to estimate dipole effects on the IE using an linear model equation. The resulting dipole correction did not improve our correlations.
    - ❖((Chemsol IE) – IE) / ((Chemsol dipole) – dipole) = slope of equation; the intercept is the IE with no dipole effects
- ❖Nickel
  - ❖Calculated the core IEs for Ni and H_2Ni with various models, and used NWChem to calculate relativistic corrections for Ni to see if they are important contributors.
    - ❖(Relativistic IE) – (Non-relativistic IE) = relativistic correction
  - ❖In order to find the best density functional to run the H_2Ni(ligand) calculations, I calculated Ni core IEs with cc-pVQZ basis set and 82 different density-functionals.
    - ❖Density-functional effects are very nearly additive, so I used calculations for 15 combinations (exchange+correlation) and 18 hybrids to calculate the remaining combinations.
    - ❖Comparing the percent errors of the density-functionals from experimental values, I determined that the BOP hybrid is the most accurate to calculate Ni core IE shifts.

Conclusions

❖By calculating the percent differences between our calculated IE values for nickel atom and experimental values, we determined that the BOP hybrid density-functional is the most accurate for our nickel calculations.

❖There is a polynomial correlation between the IE shift and both the partial charge and percent ionicity in copper.

Acknowledgements

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References

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❖4. WebMO http://www.webmo.net

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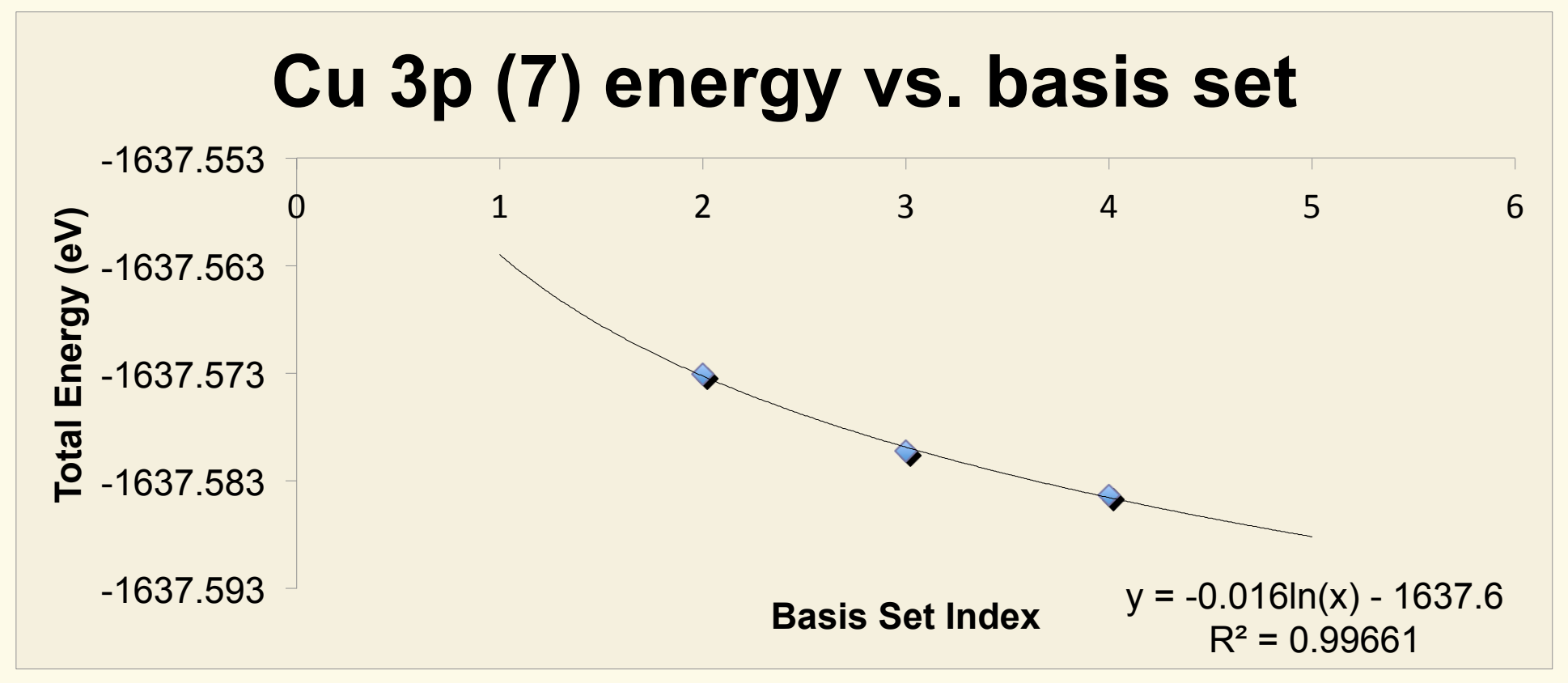
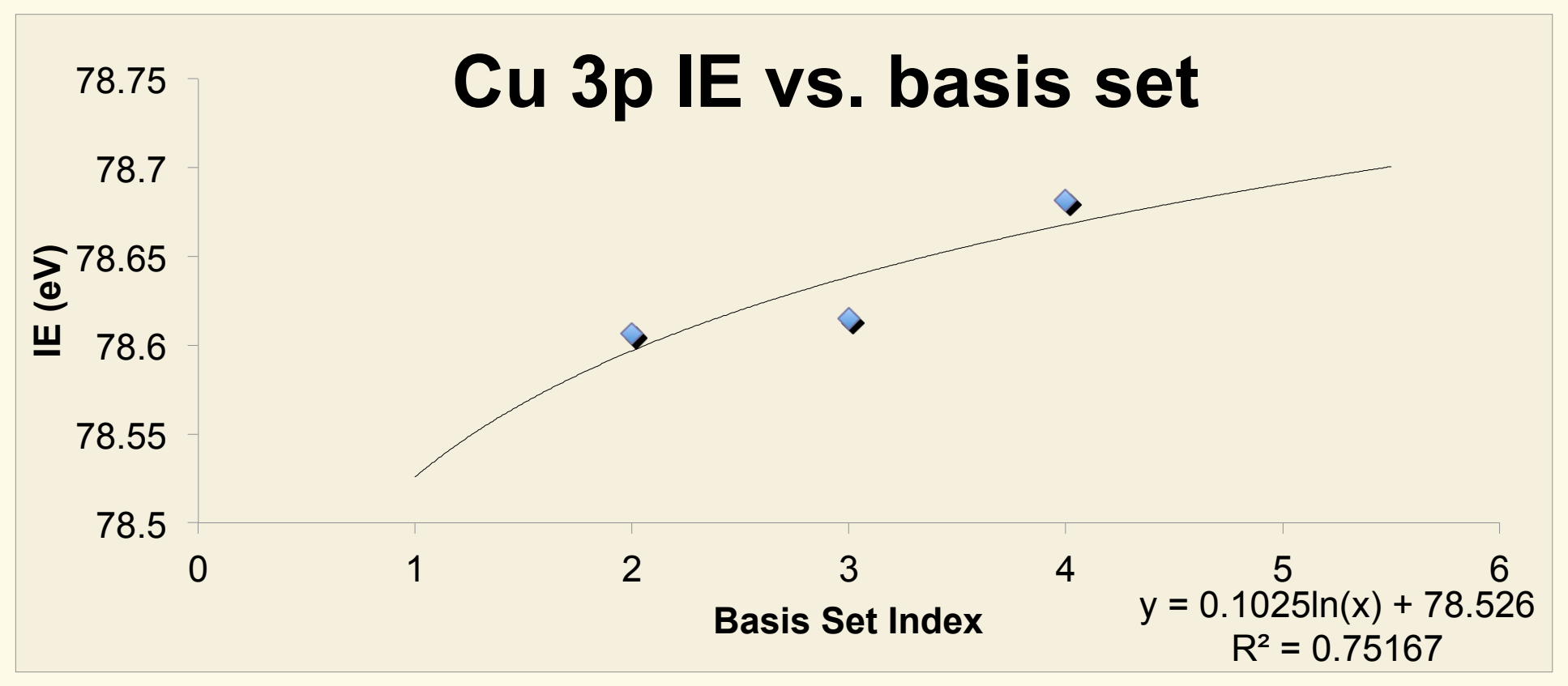
❖6. NWChem 5.1 Software. Described in article: Computational Physics Communications *181*, **2010**, 1477.

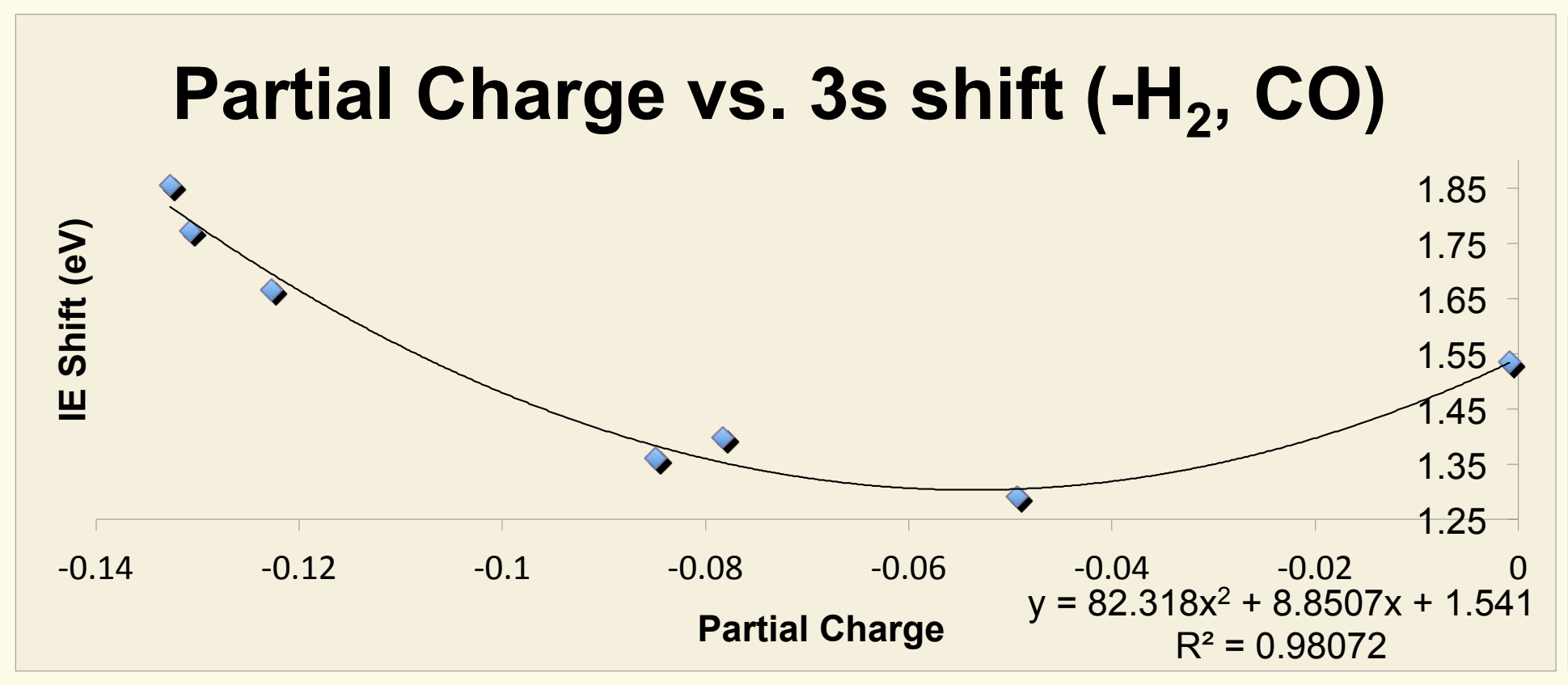
Results and Discussion

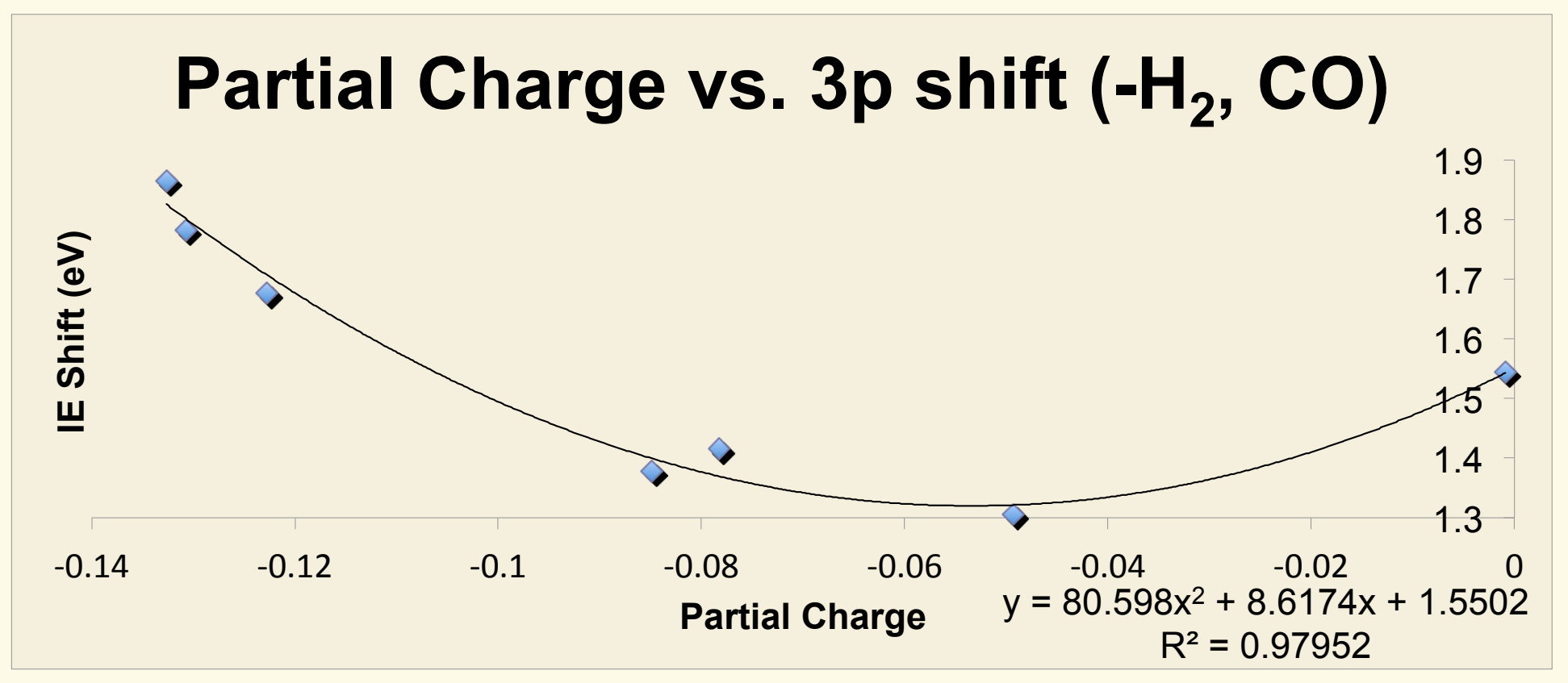




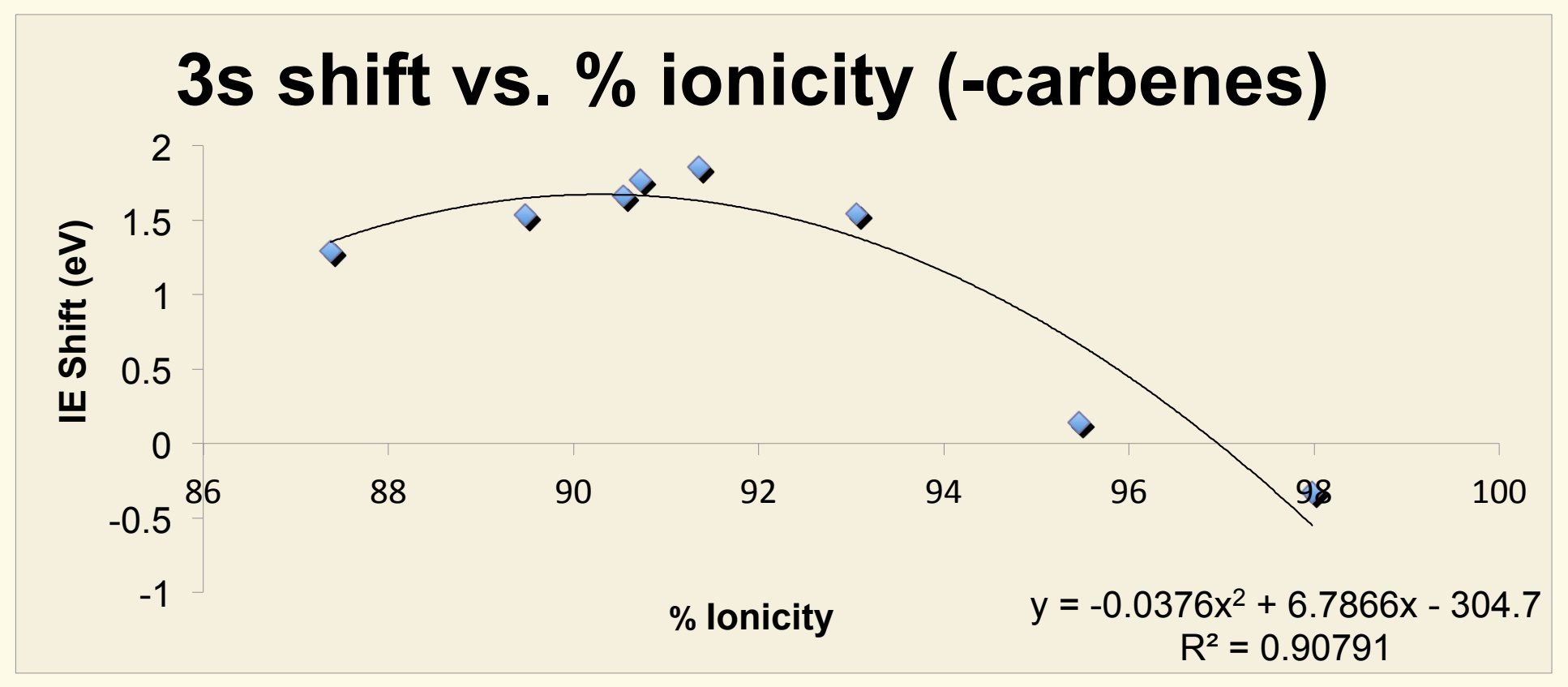
❖Graphing calculated energy versus basis set produces a log function.

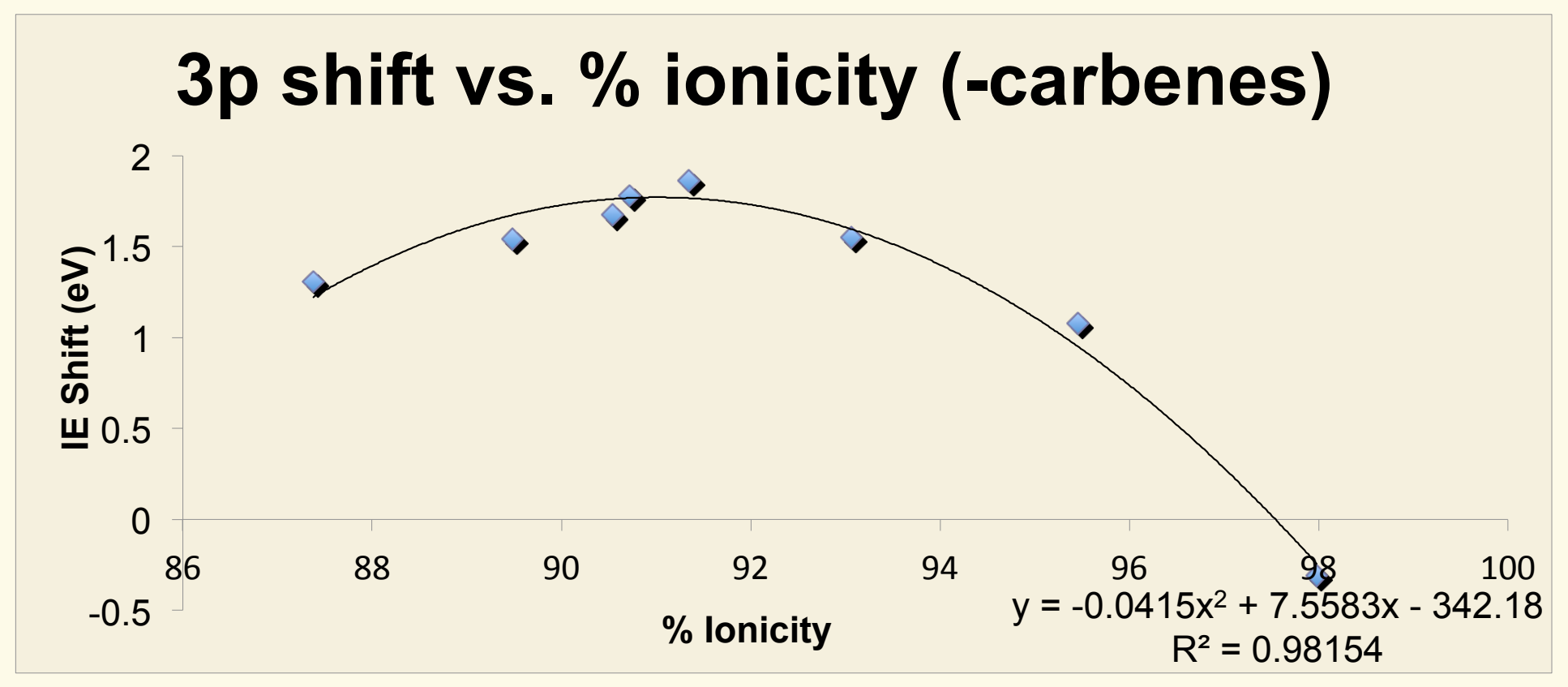
❖Graphing IE's by basis set should produce a log function, but I need 5Z results.





❖Partial charge on copper is parabolically correlated with IE shift in copper, once H_2 and CO values are removed.





❖Percent ionicity of the metal-ligand bond is parabolically correlated with IE shift in copper, once hydroxymethyl carbene and methoxycarbene are removed.

❖Analyzing the percent error of each density-functional shows that the density-functionals highlighted in yellow are the most accurate overall.

❖The calculations highlighted in red did not converge.

Density-Functional combinations: sum of % errors in each shell (2s, 2p, 3s, 3p)

	Slater-Dirac	Becke86	PW86	Becke88	Gill96	Becke(EDF1)	Perdew91	PBE
vokso-wilk-nusair	14.08	13.16	19.21	20.11	20.52	13.34	13.39	13.29
perdew-zunger	24.08	20.34	43.25	44.14	44.56	20.69	20.31	20.38
wigner	25.76	21.80	44.93	45.83	46.25	22.15	21.78	21.84
perdew-wang 92	22.68	23.28	28.02	28.98	29.43	23.47	23.52	23.42
lee-yang-parr	26.00	30.45	13.17	13.30	13.29	30.12	30.58	30.43
perdew86	12.41	13.01	18.91	19.86	20.32	13.19	13.25	13.14
LYP refit	24.42	26.36	10.62	10.81	10.82	26.12	26.48	26.37
PW91	13.50	14.10	20.11	21.07	21.52	14.28	14.34	14.23

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	M06-2X	BR89/B94	BR89/PK06	M06-HF	M06-L	M05	BOP	BECKE97-1
2s	2.63	2.35	1.71	2.17	2.61	1.50	2.37	3.09	2.58
2p3	-0.42	-0.49	-1.47	-0.76	99.02	-1.38	-0.39	-0.34	-0.41
2p4	-0.37	-0.49	-1.47	-0.76	99.02	-1.35	-0.39	-0.27	-0.41
2p5	-0.37	-0.46	-1.47	-0.76	99.02	-1.35	-0.31	-0.27	-0.36
3s	0.12	-1.15	-5.02	-1.58	-0.25	-6.20	-0.87	2.08	0.06
3p7	-8.47	-10.06	-16.86	-9.84	87.41	-16.33	-9.24	-7.57	-8.68
3p8	-8.37	86.82	-17.05	-9.84	-10.27	-16.32	-9.14	-6.56	-8.68
3p9	-8.37	-10.11	-17.05	-10.05	-9.95	-16.31	-9.14	-6.56	-8.29
sum each shell	11.64	14.04	25.07	14.35	189.28	25.41	12.88	13.09	11.73
sum all orbitals	29.11	111.93	62.12	35.76	407.55	60.74	31.85	26.75	29.46

	BECKE97	PBE96	B3LYPoriginal	B3LYP	M05-2X	BECKE97-2	EDF1	M06	EDF2
2s	2.62	2.53	2.63	2.35	2.33	2.54	3.05	2.19	2.65
2p3	-0.41	-0.39	-0.44	98.94	98.97	-0.41	-0.39	-0.68	-0.52
2p4	98.94	-0.39	-0.38	-0.39	98.97	-0.53	-0.31	-0.68	-0.52
2p5	-0.36	-0.34	98.95	98.94	98.97	-0.46	-0.31	100.00	-0.47
3s	0.19	-0.32	0.27	0.12	-0.81	-0.12	1.80	100.00	0.43
3p7	-8.49	-8.79	-8.38	-8.53	-9.62	-8.81	-7.79	-9.44	-8.64
3p8	-8.49	-8.79	-8.16	-8.37	-9.62	-8.81	-6.90	100.00	-8.64
3p9	-8.20	-8.60	-8.16	-8.31	-9.86	-8.57	-6.90	-9.55	-8.13
sum each shell	11.72	12.03	11.71	109.94	111.73	11.87	13.02	112.32	12.25
sum all orbitals	127.72	30.15	127.36	225.94	329.15	30.23	27.42	322.54	30.02

Future Study

- ❖Continue calculations on nickel complexes
- ❖Determine the linear contributors to the parabolic correlations we saw in copper, and if this correlation is present in Ni compounds
- ❖Obtain more accurate relativistic corrections using NWChem
- ❖Run MP3 and MP4 calculations on Nickel atom
- ❖Run cc-pV5Z calculations on H_2Ni in order to determine an equation to accurately extrapolate our IE values