Core Electron Binding Energy Shifts in Transition Metal Hydrides

**Project Goals:**

Build a Computational Model
Predict core electron binding energy (CEBE) shifts
Correlate these shifts to changes in complex structure

**Complex Structure, L:->M-H:**

How does the coordination environment shift the metal CEBE?
• Do changes in coordination number result in substantial shifts?
• How does this differ from coordination compounds without H?
Motivation

Transition metal hydrides are used as catalysts for a variety of reactions involving hydrogen.

• Ligands are designed to improve catalysis.
• Catalyst structure, and structure-function relationships, are not always well understood.
• Computational models can predict structure and function, for many complex geometries.
• Experimental methods such as X-ray absorption are used to obtain core electron binding energies.
• Quantum calculations can predict metal core electron binding energies, and correlate these to structural features in potential catalysts.
Background – X-ray Absorption Spectra

Exact energy ejects a core electron at the core electron binding energy (CEBE). This is the X-ray photoelectron spectrum (XPS). Other X-ray absorption data include:

• Core excitations occur near the core ionization energy. This is the near-edge spectrum (XANES).
• At higher X-ray energies, the photoelectron scatters from neighboring atoms. This is the extended fine structure (EXAFS).
Background – CEBE Shifts

Core electron binding energies (CEBE) for a given atom are affected by the chemical environment of that atom. These effects are called chemical shifts.

Commonly observed contributors to chemical shifts:\(^1,^2\)

- Charge on the atom of interest (often assumed to be the dominant contribution)
- Electric field due to surrounding ions (or partial charges on surrounding atoms)

\[
\sigma_M = kq_M + m\sum_j \left( \frac{q_j}{r_{Mj}} \right) + b_M
\]

Charge effect
Electric field effect
Other effects

Background – Ligand Additivity

Substantial, roughly additive shifts in transition metal CEBE’s due to ligand binding have been reported for coordination complexes\textsuperscript{1,2,3}.

• Negative shifts are observed for σ-donor ligands.
• Positive shifts are observed for π-acceptor ligands.
• Shifts are roughly proportional to the number of bound ligands of each type (ligand additivity).

Does the covalency of the metal-hydride bond alter ligand binding contributions to metal CEBE shifts?

Building a Model

We will study complexes of the form LCuH, LNiH$_2$, L$_2$NiH$_2$, LCoH$_3$, L$_2$CoH$_3$, and L$_3$CoH$_3$:

• All hydride ligands are covalently bound to the metal, and no hydride ligands are oriented \textit{trans} to a metal-hydride bond.

• All coordinated ligands L are neutral.

• There is at most one coordinated ligand L per hydrogen, and all coordinated ligands are oriented \textit{trans} to a metal-hydride bond.
Building a Model

Previous calculations in our group used these methods:

\[ \Delta \text{Kohn-Sham CEBE} = E(\text{Core ionized}) - E(\text{Ground state}) \]

Density Functionals and Basis Sets:
• M06-L hybrid functional performed well for Ni atom
• Absolute errors were >1eV for Ni atom
• Basis set errors in chemical shifts were <1 eV for the cc-pVTZ basis

Relativistic Corrections:
• Douglas-Kroll-Hess scalar correction in NWChem improved absolute errors significantly for Ni atom, but did not affect the error in chemical shifts.
Building a Model

Our computational methodology will evolve from previous work in our group:

\[ \Delta \text{Kohn-Sham CEBE} = E(\text{Core ionized}) - E(\text{Ground state}) \]

- Accuracy of predicted Cu and Co core electron binding energies will be compared across density functionals, against experimental data.
- Scalar relativistic corrections will be computed for Cu and Co core electron binding energies and chemical shifts, to evaluate this possible source of error.
- Basis set error will be assessed for Dunning-type basis sets of different sizes.
Predicting CEBE Shifts

A previous student in our group (J. Jorstad) calculated CEBE shifts for nickel hydride complexes, relative to $\text{H}_2\text{Ni}$:

- CEBE shifts were similar for $2s$, $2p$, $3s$, $3p$ core orbitals.
- Significant, roughly additive chemical shifts were predicted.

\[
\begin{array}{|c|c|c|c|c|}
\hline
\text{Complex} & \sigma_{2s} & \text{Avg. } \sigma_{2p} & \sigma_{3s} & \text{Avg. } \sigma_{3p} \\
\hline
\text{H}_2\text{Ni}(\text{PH}_3) & -1.00 & -1.10 & -1.02 & -1.15 \\
\text{H}_2\text{Ni}(\text{PH}_3)_2 & -1.36 & -1.39 & -1.43 & -1.51 \\
\text{H}_2\text{Ni}(\text{NH}_3) & -1.32 & -1.42 & -1.39 & -1.52 \\
\text{H}_2\text{Ni}(\text{NH}_3)_2 & -2.14 & -2.16 & -2.29 & -2.31 \\
\text{H}_2\text{Ni}(\text{CH}_3\text{CN}) & -1.54 & -1.63 & -1.54 & -1.67 \\
\text{H}_2\text{Ni}(\text{CH}_3\text{CN})_2 & -2.23 & -2.26 & -2.31 & -2.36 \\
\text{H}_2\text{Ni}(\text{CO})_2 & 1.30 & 1.18 & 1.19 & 1.08 \\
\hline
\end{array}
\]
Predicting CEBE Shifts

We will calculate CEBE shifts for copper, nickel, and cobalt hydride complexes, relative to HCu, H₂Ni, and H₃Co:

- CEBE shifts will be predicted for 2s, 2p, 3s, 3p core orbitals.
- More π-acceptor ligands will be included in the study.
- Ligand contributions will be compared to those found experimentally by Feltham and Brant for coordination complexes (without hydride ligands).
- CEBE shifts will also be calculated for selected coordination complexes, to establish a direct comparison with Feltham and Brant’s reported experimental values.

Does M—H bonding significantly alter ligand binding contributions to metal CEBE shifts?
CEBE Shifts and Complex Structure

Analysis of calculations by a previous student in our group (J. Jorstad) suggests that \( \pi \)-backbonding quantitatively affects ligand contributions to CEBE shifts.

- Not all calculated CEBE shifts could be fit reliably to an empirical model equation of the following form:
  \[
  \sigma_M = k q_M + m \sum_j \left( \frac{q_j}{r_{M_j}} \right) + b_M
  \]
  – Notably, \( \pi \)-acceptor complexes were outliers in the fit.

- NBO 2\textsuperscript{nd} order perturbation analysis was used to quantify metal\( \rightarrow \)ligand charge transfer energy for each ligand; this term was then added to the empirical model.
  \[
  \sigma_M = k q_M + \left[ m \sum_j \left( \frac{q_j}{r_{M_j}} \right) - p \sum_i E_i^{MLCT} \right] + b_M
  \]
  – Calculated CEBE shifts were fit to the new model with \( R^2 = 0.97 \).
CEBE Shifts and Complex Structure

We will analyze calculated ligand contributions to CEBE shifts, to explore the role of \( \pi \)-backbonding.

- NBO 2\textsuperscript{nd} order perturbation analysis will be used to quantify metal\( \rightarrow \)ligand charge transfer.
- All shifts will be fit to the expanded empirical model, to validate the fit against a larger data set.
- Metal\( \rightarrow \)ligand charge transfer will be compared for complexes with and without hydride ligands.

*Does the covalency of the metal-hydride bond alter the extent of \( \pi \)-backbonding to coordinated ligands?*
Summary

Metal core electron binding energies (CEBE) for metal hydride complexes will be modeled using DFT.

• These calculations will predict the shifts in CEBE due to different ligands, especially $\pi$-acceptor ligands.

• The shifts will be analyzed to determine the effect of the metal—hydride bond on these shifts.

• The calculations will also be analyzed to understand the effect of metal $\rightarrow$ ligand charge transfer.

• These analyses will be combined to try to explain how covalent metal—hydride bonds may alter the effects of coordinated ligands on the metal CEBE.