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RESEARCH ARTICLE

# Δ-SCF calculations of core electron binding energies in first-row transition metal atoms

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## Abstract

Core electron binding energies (CEBE) of nickel and copper atoms have been calculated using single-configuration energy differences, the so-called Δ-self-consistent field (Δ-SCF) method. Basis set convergence has been examined for calculated L-shell and M-shell core electron binding energies, and a wide array of density functionals have been evaluated. Scalar relativistic corrections have been estimated using the popular Douglas-Kroll-Hess (DKH) approximation. While basis set convergence and functional dependence mirror the behavior reported in the literature for main group elements, the simplest Δ-SCF calculations with pure Hartree-Fock (HF) exchange and no correlation surprisingly outperform all density functionals in reproducing free-atom CEBE values for Ni and Cu.

KEYWORDS

core electron binding energies, delta-SCF, density functionals, Douglas-Kroll-Hess (DKH), transition metals

## 1 | INTRODUCTION

### 1.1 | Δ-SCF and related methods

The Δ-self-consistent field (Δ-SCF) method, also referred to as the ΔKohn-Sham (Δ-KS) method when used with density functionals, accurately predicts core electron binding energies (CEBE) of lighter elements in a variety of molecules [1–6, 9]. Such calculations are facilitated by using the maximum overlap method to prevent the collapse of a core-ionized Slater determinant [3, 10].

Cavigliasso and Chong showed that Δ-KS calculations using core-valence correlated Dunning-style basis sets could reproduce 1*s* CEBE values for main-group, second row nonmetal atoms such as B, C, N, O, and F in small molecules [1]. Besley, Gilbert, and Gill demonstrated that reasonable accuracy also could be obtained with uncontracted Pople-style basis sets, and that the method could be applied successfully to copper (II) ions in coordination compounds [3]. Fouda and Besley showed that the improved description of core electrons by IGLO-type basis sets could be leveraged to yield accurate CEBE values of first-row and second-row atoms in small molecules [4]. However, Takahashi and Petersson among others have noted a dependence of such calculations on the choice of density functionals, finding the description of exchange to be particularly important [2]. More recently, Hait and Head-Gordon showed that the SCAN meta-GGA functional and the wB97X-V range-separated hybrid functional yield accurate CEBE values for these lighter elements in small molecules, albeit without relativistic corrections [5]. A recent review by Norman and Dreuw noted that when density functionals are used, the self-interaction error (SIE) must be larger for core electrons than for valence electrons and thus should affect the description of CEBE values [6]. One approach to address the difference in SIE for heavier elements is to use a short-range corrected functional parameterized for core excitations by Besley and others [7]. Even so, increased accuracy is not guaranteed, and relativistic corrections also must be considered [8]. Accurate prediction of CEBE values within the Δ-KS approach therefore should not be taken for granted, and should be re-examined whenever differences in exchange energy and/or SIE are expected to be larger than in previously benchmarked data sets. Indeed, Besley's most recent review warns that conclusions drawn from benchmarking on lighter nuclei may not apply to heavier nuclei, noting that Δ-KS performance for core ionization energies differs dramatically from the first row to the second row of the periodic table [9].

Δ-SCF calculations are simple enough in principle and practice to be applied straightforwardly to core electron binding energies of transition metal atoms and ions [3]. Such an approach is appealing not only for the practicality of its implementation, but also for its conceptual simplicity. Core-ionized state energies and ground-state energies are calculated separately at the same level of theory, and their difference is taken to represent the core electron binding energy. The use of two separate calculations allows for orbital relaxation in the core-ionized state as well as in the ground state. The core-ionized state wavefunction is targeted by a core-ionized initial guess, and variational collapse to the ground state is prevented by an algorithm such as the maximum-overlap method [3, 10]. Resulting core ionization energies typically are much more accurate than those predicted by time-dependent density functional theory (TD-DFT), a widely used method in which orbitals are optimized only for the ground state [5]. For the first-row transition metal atoms that are the focus of the present study, L-shell (2*s* and 2*p*) and M-shell (3*s* and 3*p*) CEBE values have been calculated by calculating energies for the core-ionized states and subtracting the ground state energy from each of these. The Δ-SCF approach can be extended in a straightforward manner from first-row transition metal atoms to their molecules or complexes, and the relative core electron binding energies can be used to predict transferable chemical shifts across related species. Chemical shifts may then be attributed to the metal oxidation state, and/or to subtler effects of the coordination environment on the electronic structure of the metal atom. Relative to the free-atom calculations reported here, performance should improve when applied to the prediction of chemical shifts due to cancellation of systematic errors in predicted binding energies. The present work aims to evaluate the performance of these methods when predicting absolute CEBE values of first-row transition metal atoms, and by extension to provide upper bounds to the error in predicted chemical shifts.

## 1.2 | Density functionals and basis sets for core electron binding energies

Δ-SCF calculations of core ionization energies usually employ density functionals that have been optimized for ground-state calculations. These can be expected to capture some effects of dynamic correlation on the ground state, but may not capture as much on a core-ionized state. On the other hand, density functional methods may introduce a smaller self-interaction error (SIE) in the calculation of a core-ionized state than on the ground state [6]. Therefore, accurate prediction of CEBE values with the Δ-SCF method may depend on a delicate balance of approximations not anticipated in the development of widely used density functionals. Various density functionals have been reported to yield acceptable estimates of CEBE values in light atoms by the Δ-SCF method [1, 11–13]. Some families of density functionals, such as local spin-density approximation (LSDA) or range-separated hybrid (RSH) functionals with default parameters may not perform as well, but the converse does not follow: no family of density functionals performs well uniformly [11]. The aggressively parameterized Minnesota functionals often outperform other functionals within a given family, with the meta-GGA functional M06-L standing out in one survey [12]. While existing benchmarking studies of Δ-SCF calculations of core ionization energies have focused on lighter main-group atoms, transition metal atoms may require a different balance of approximations.

Basis sets to be used in Δ-SCF calculations should offer adequate flexibility to describe both the ground and core-ionized state wavefunctions. Basis sets optimized for ground-state and valence-excited state calculations may not offer much flexibility in describing core electrons, which limits their usefulness in describing core-ionized state wavefunctions. One approach to address this issue is to uncontract the core basis functions of standard atom-centered basis sets [3]. Another is to add in core functions from the atom with the next higher atomic number ($Z + 1$) to approximately describe the loss of shielding to remaining core electrons upon ionization [14]. A third approach is to use core-valence polarized, correlation consistent basis sets (cc-pCVnZ) or uncontracted, core-interpolated, polarization-consistent basis sets (pcX-n) [15, 16]. IGLO-type basis sets developed for NMR calculations also may be applied [4]. A recent survey in the literature found the cc-pCVTZ basis to provide a good balance between cost and accuracy for Δ-SCF calculations of core ionization energies in light atoms, and the cc-pwCVnZ basis sets are parameterized in the same way for first-row transition metal atoms [4].

## 1.3 | Scalar relativistic corrections

Relativistic corrections must be considered when calculating CEBE values of heavier atoms [17]. Even a scalar relativistic correction substantially reduces the systematic underestimation of CEBE values within the Δ-SCF approach. Explicit relativistic calculations of spin-orbit coupling could be used to predict multiplet splitting in 2*p* and 3*p* core ionization spectra, but this is beyond the scope of the present work. The Douglas-Kroll-Hess approach to calculate scalar relativistic corrections as implemented in NWChem may be straightforwardly applied to calculate energy levels in first-row transition metal atoms, when using the appropriately contracted basis sets [18–20]. Corrections thus obtained in the present work fell within $\approx 1$ eV of those previously reported in the literature for 2*s* core ionization of copper and nickel atoms [17, 21].

### 1.4 | Core electron binding energies of transition metal atoms

Transition metal atoms and ions can possess multiple low-lying states, due to their large number of valence electrons and unpaired valence electrons. For core-ionized free atoms, the presence of these low-lying states may complicate the interpretation of experimental photoionization spectra as well as the convergence and complexity of quantum chemical calculations [22–25]. Late-transition metal nickel and copper atoms were chosen for the present study, because of their potential to form stable, low-valent organometallic and coordination complexes. These two atoms also offer a contrast between the most complex (Ni) and least complex (Cu) photoelectron spectra among first-row transition metals.

Nickel atoms have a ground state valence electron configuration of $4s^{2}3d^{8}$, and a low-lying excited state valence electron configuration of $4s^{1}3d^{9}$. For core-ionized nickel atoms, the order of energies for these two valence electron configurations is reversed [23]. At the elevated temperatures required to atomize nickel, population of low-lying states of both neutral and core-ionized nickel atoms gives rise to a complex multiplet structure in the regions of photoionization spectra attributed to $2p$ and $3p$ core ionization [26, 27]. Thus in addition to the $2p_{1/2}$, $2p_{3/2}$ multiplet splitting due to spin-orbit coupling, further splitting on the order of a few eV may be attributed to states with different electron configurations at these elevated temperatures.

Copper atoms have a ground state valence electron configuration of $4s^{1}3d^{10}$, which does not change upon core ionization. Their photoelectron spectra do not exhibit the more complex multiplet structure observed for nickel atoms, even at elevated temperatures [24, 25]. Only the $2p_{1/2}$, $2p_{3/2}$ multiplet splitting due to spin-orbit coupling is observed.

For the present work, calculated CEBE values were compared to empirical free-atom values from the literature, using the appropriate weighted average to combine the reported $2p_{1/2}$, $2p_{3/2}$ multiplet energies into a single $2p$ core electron binding energy [28]. These empirical values are within a few eV of those reported more recently for atomic photoelectron spectra of nickel and copper atoms, and permit both nickel and copper atoms to be treated in a consistent manner despite the difference in complexity of their photoelectron spectra [24, 25]. For the nickel atom $2p$ and $3p$ multiplets, this choice eliminates the added complexity associated with thermal population of multiple low-lying states in more recently measured atomic spectra. Small and subtle differences between measured values in the literature are beyond the scope of the present work, and would not substantially affect its conclusions.

## 2 | COMPUTATIONAL METHODS

### 2.1 | Δ-SCF calculations

The Δ-SCF approach was used to calculate $2s$, $2p$, $3s$, and $3p$ core electron binding energies of nickel and copper atoms within the framework of single-configuration quantum chemical calculations. This approach uses standard ground-state, single determinant methods to calculate the ground state and the core-ionized state energy, and takes the difference in energy to represent the core ionization energy. The maximum-overlap method (MOM), as implemented in both Q-Chem and in the DFT module of NWChem, was used to ensure convergence on selected

**TABLE 1** Restricted open-shell and spin-unrestricted Hartree-Fock core electron binding energies in eV, with the cc-pwCVTZ basis set

| Nickel atom | Non-relativistic | Non-relativistic | Relativistic | Relativistic |
|---|---|---|---|---|
| Core hole | CEBE (ROHF) | CEBE (UHF) | CEBE (ROHF) | CEBE (UHF) |
| $2s$ | 1001.1 | 1001.1 | 1020.5 | 1020.5 |
| $2p$ | 864.1 | 863.9 | 868.3 | 868.1 |
| $3s$ | 119.0 | 118.9 | 122.4 | 122.4 |
| $3p$ | 74.6 | 74.6 | 75.7 | 75.7 |
| **Copper atom** | **Non-relativistic** | **Non-relativistic** | **Relativistic** | **Relativistic** |
| **Core hole** | **CEBE (ROHF)** | **CEBE (UHF)** | **CEBE (ROHF)** | **CEBE (UHF)** |
| $2s$ | 1084.7 | 1084.6 | 1107.1 | 1107.0 |
| $2p$ | 941.5 | 941.2 | 946.2 | 945.9 |
| $3s$ | 128.3 | 128.2 | 132.0 | 131.9 |
| $3p$ | 82.9 | 82.8 | 83.8 | 83.6 |

*Note*: The Hartree-Fock method was used with and without Douglas-Kroll-Hess (DKH) scalar relativistic corrections, within the DFT module of NWChem.

core-ionized determinants [3, 10]. Reported results were based on spin-unrestricted calculations, and restricted open-shell Hartree-Fock calculations were performed for comparison as shown in Table 1. Restricted open-shell and unrestricted Hartree-Fock calculations of core electron binding energies agree to within a few tenths of an eV. Values of $\langle S^2 \rangle$ are consistent with minimal spin contamination, and are listed in the Supporting information for all reported calculations.

Energy differences were taken between the lowest-energy single determinants of neutral atoms and of core-ionized atoms at a given level of theory. Eigenvectors were printed out to verify the electron configuration for each calculation. The ground state HF/cc-pwCVTZ energy obtained for neutral nickel atoms corresponds to the $[\mathrm{Ar}]4s^{2}3d^{8}$ electron configuration as expected, but when calculated with MP2 and some density functionals, an electron configuration of $[\mathrm{Ar}]4s^{1}3d^{9}$ was found to be lower in energy. The valence electron configuration of $4s^{1}3d^{9}$ also is associated with the lowest energy core-ionized states. Thus, CEBE values calculated for the nickel atom may or may not include the energy associated with a change in valence electron configuration. This contribution to the calculated binding energy, when present, is not large enough to alter the overall conclusions.

While atomic core ionization energies may be calculated to a higher level of accuracy using explicit multi-configurational wavefunction methods, and/or with a full relativistic treatment of spin-orbit coupling, such methods would be computationally expensive for larger systems [22, 23, 29]. These calculations are beyond the scope of the present work.

**TABLE 2** Basis set convergence, for nickel and copper atom 2*s*, 2*p*, 3*s*, and 3*p* core electron binding energies in eV

| Basis set | Relativistic | Ni 2*s* | Ni 2*p* | Ni 3*s* | Ni 3*p* |
|---|---|---|---|---|---|
| cc-pVDZ | – | 1003.1 | 866.9 | 119.0 | 74.8 |
| cc-pVTZ | – | 1002.3 | 865.9 | 119.0 | 74.7 |
| cc-pVQZ | – | 1001.7 | 865.0 | 119.0 | 74.6 |
| cc-pV5Z | – | 1001.3 | 864.5 | 118.9 | 74.6 |
| cc-pwCVTZ | – | 1001.1 | 863.9 | 118.9 | 74.6 |
| cc-pwCVQZ | – | 1001.0 | 863.8 | 118.9 | 74.6 |
| cc-pwCV5Z | – | 1001.0 | 863.8 | 118.9 | 74.6 |
| cc-pVDZ-DK | DKH | 1022.7 | 871.3 | 122.4 | 75.9 |
| cc-pVTZ-DK | DKH | 1021.9 | 870.1 | 122.4 | 75.7 |
| cc-pVQZ-DK | DKH | 1021.2 | 869.3 | 122.4 | 75.7 |
| cc-pV5Z-DK | DKH | 1020.8 | 868.7 | 122.4 | 75.7 |
| cc-pwCVTZ-DK | DKH | 1020.5 | 868.1 | 122.4 | 75.7 |
| cc-pwCVQZ-DK | DKH | 1020.5 | 868.1 | 122.4 | 75.7 |
| cc-pwCV5Z-DK | DKH | 1020.4 | 868.0 | 122.4 | 75.7 |
| Expt. [28] | N/A | 1024 | 876 | 125 | 82 |
| **Basis set** | **Relativistic** | **Cu 2*s*** | **Cu 2*p*** | **Cu 3*s*** | **Cu 3*p*** |
| cc-pVDZ | – | 1086.7 | 944.2 | 128.3 | 82.9 |
| cc-pVTZ | – | 1085.8 | 943.0 | 128.2 | 82.8 |
| cc-pVQZ | – | 1085.3 | 942.3 | 128.2 | 82.8 |
| cc-pV5Z | – | 1084.9 | 941.7 | 128.2 | 82.8 |
| cc-pwCVTZ | – | 1084.6 | 941.2 | 128.2 | 82.8 |
| cc-pwCVQZ | – | 1084.6 | 941.1 | 128.2 | 82.8 |
| cc-pwCV5Z | – | 1084.6 | 941.1 | 128.2 | 82.8 |
| cc-pVDZ-DK | DKH | 1109.2 | 949.1 | 131.9 | 83.8 |
| cc-pVTZ-DK | DKH | 1108.3 | 947.8 | 131.9 | 83.7 |
| cc-pVQZ-DK | DKH | 1107.7 | 947.0 | 131.9 | 83.7 |
| cc-pV5Z-DK | DKH | 1107.4 | 946.5 | 131.9 | 83.6 |
| cc-pwCVTZ-DK | DKH | 1107.0 | 945.9 | 131.9 | 83.6 |
| cc-pwCVQZ-DK | DKH | 1107.0 | 945.9 | 131.9 | 83.6 |
| cc-pwCV5Z-DK | DKH | 1107.0 | 945.9 | 131.9 | 83.6 |
| Expt. [28] | N/A | 1105.7 | 947.0 | 128.8 | 83 |

*Note*: The Hartree-Fock method was used with and without Douglas-Kroll-Hess (DKH) scalar relativistic corrections, within NWChem.

## 2.2 | Basis sets and density functionals

The Hartree-Fock (HF) method was used as implemented in Q-Chem and as exact exchange within the DFT module of NWChem [18, 30]. MP2 calculations were performed as implemented in Q-Chem using the resolution of identity approximation (RI-MP2) to reduce the computational cost [31]. Density functionals of different types were evaluated: LSDA, GGA, meta-GGA, and hybrid, using the default standard grids as implemented in Q-Chem [30, 32, 33]. Relativistic corrections were evaluated for Hartree-Fock exact exchange and selected density functionals as implemented in NWChem, using fine grids for Minnesota functionals and medium grids for all others. Range-separated hybrid functionals were not considered.

Correlation-consistent cc-pV*n*Z and cc-pwCV*n*Z-NR basis sets were used to assess basis set convergence for non-relativistic calculations, and the corresponding cc-pV*n*Z-DK and cc-pwCV*n*Z-DK relativistic basis sets were used for scalar relativistic calculations [16]. For RI-MP2 calculations, the associated RI-cc-pwCV*n*Z-NR basis sets were used as auxiliary basis functions.

## 2.3 | Scalar relativistic corrections

Hartree-Fock Δ-SCF calculations reported in this work were carried out with and without Douglas-Kroll-Hess scalar relativistic corrections as implemented in NWChem, and their differences were taken as estimates of the relativistic correction for a given core electron binding energy [18, 19]. These differences were found to be nearly independent of the basis set employed (Table 3). Relativistic corrections also were calculated in the same manner with a few selected density functionals, and were found to be similar to the corresponding values from Hartree-Fock calculations (Table 3).

**TABLE 3** Scalar relativistic corrections, for nickel and copper atom 2*s*, 2*p*, 3*s*, and 3*p* core electron binding energies in eV

| Basis sets | Method | Ni 2*s* | Ni 2*p* | Ni 3*s* | Ni 3*p* |
|---|---|---|---|---|---|
| cc-pVDZ, cc-pVDZ-DK | HF | 19.6 | 4.3 | 3.4 | 1.1 |
| cc-pVTZ, cc-pVTZ-DK | HF | 19.5 | 4.3 | 3.4 | 1.1 |
| cc-pVQZ, cc-pVQZ-DK | HF | 19.5 | 4.3 | 3.4 | 1.1 |
| cc-pV5Z, cc-pV5Z-DK | HF | 19.5 | 4.3 | 3.4 | 1.1 |
| cc-pwCVTZ, cc-pwCVTZ-DK | HF | 19.5 | 4.2 | 3.4 | 1.1 |
| cc-pwCVQZ, cc-pwCVQZ-DK | HF | 19.4 | 4.2 | 3.4 | 1.1 |
| cc-pwCV5Z, cc-pwCV5Z-DK | HF | 19.4 | 4.2 | 3.4 | 1.1 |
| cc-pVQZ, cc-pVQZ-DK | BOP (med. grid) | 18.9 | 4.1 | 3.1 | 0.8 |
| cc-pwCVTZ, cc-pwCVTZ-DK | BOP (med. grid) | 18.8 | 3.9 | 3.0 | 0.8 |
| cc-pVQZ, cc-pVQZ-DK | M06-L (fine grid) | 19.1 | 4.2 | 3.2 | 1.0 |
| cc-pwCVTZ, cc-pwCVTZ-DK | M06-L (fine grid) | 19.0 | 4.2 | 3.2 | 0.7 |
| Lit. [17] | MC-DBF | 18.2 | – | – | – |
| **Basis sets** | **Method** | **Cu 2*s*** | **Cu 2*p*** | **Cu 3*s*** | **Cu 3*p*** |
| cc-pVDZ, cc-pVDZ-DK | HF | 22.5 | 4.8 | 3.6 | 0.9 |
| cc-pVTZ, cc-pVTZ-DK | HF | 22.5 | 4.8 | 3.6 | 0.9 |
| cc-pVQZ, cc-pVQZ-DK | HF | 22.4 | 4.8 | 3.6 | 0.9 |
| cc-pV5Z, cc-pV5Z-DK | HF | 22.4 | 4.8 | 3.6 | 0.9 |
| cc-pwCVTZ, cc-pwCVTZ-DK | HF | 22.4 | 4.7 | 3.6 | 0.9 |
| cc-pwCVQZ, cc-pwCVQZ-DK | HF | 22.4 | 4.7 | 3.6 | 0.9 |
| cc-pwCV5Z, cc-pwCV5Z-DK | HF | 22.4 | 4.7 | 3.6 | 0.9 |
| cc-pVQZ, cc-pVQZ-DK | BOP (med. grid) | 22.2 | 4.9 | 3.6 | 0.9 |
| cc-pwCVTZ, cc-pwCVTZ-DK | BOP (med. grid) | 22.1 | 4.8 | 3.6 | 0.9 |
| cc-pVQZ, cc-pVQZ-DK | M06-L (fine grid) | 22.2 | 4.9 | 3.6 | 1.0 |
| cc-pwCVTZ, cc-pwCVTZ-DK | M06-L (fine grid) | 22.1 | 4.9 | 3.6 | 1.0 |
| Lit. [17] | MC-DBF | 21.6 | – | – | – |

*Note*: Hartree-Fock exact exchange and selected density functionals were used within the DFT module of NWChem, evaluated over standard grids as indicated. Calculations were performed with and without Douglas-Kroll-Hess (DKH) scalar relativistic corrections as implemented in NWChem, to find the difference.

Thus, the relativistic correction at the Hartree-Fock level was added to non-relativistic Δ-SCF energies as a reasonable estimate when comparing the accuracy of these calculations across a large number of density functionals, an approach that has previously been reported in the literature [3].

## 3 | RESULTS AND DISCUSSION

### 3.1 | Basis set convergence and relativistic corrections

Hartree-Fock Δ-SCF calculations of core electron binding energies of nickel and copper atoms were compared for a series of correlation-consistent basis sets. Unsurprisingly, the core-valence polarized cc-pwCV*n*Z basis sets were found to be far superior to the cc-pV*n*Z basis sets for

**TABLE 4** Nickel atom core electron binding energies in eV calculated with Δ-SCF methods and the cc-pwCVTZ basis set, including a DKH scalar relativistic correction calculated at the Hartree-Fock level

| Method | Family | Ni 2*s* | Ni 2*p* | Ni 3*s* | Ni 3*p* | RMSE[a] | MUE[b] |
|---|---|---|---|---|---|---|---|
| Experiment [28] | | 1024 | 875.7 | 125 | 82 | | |
| *HF* | | *1020.5* | *868.1* | *122.4* | *75.7* | *1.4%* | *4.1* |
| RI-MP2 | | 1021.4 | 870.2 | 124.1 | 76.9 | 0.6% | 2.7 |
| Slater-VWN | LSDA | 994.8 | 864.4 | 112.1 | 72.8 | 6.0% | 14.8 |
| Slater-PZ81 | LSDA | 994.8 | 865.2 | 112.2 | 72.8 | 6.0% | 14.6 |
| Slater-PW92 | LSDA | 994.7 | 865.1 | 112.1 | 72.8 | 6.0% | 14.6 |
| Slater-Wigner | LSDA | 993.9 | 863.5 | 111.5 | 72.1 | 6.4% | 15.6 |
| B88-P86 | GGA | 996.7 | 864.0 | 112.5 | 72.8 | 5.9% | 14.3 |
| B88-PW91 | GGA | 996.4 | 863.9 | 112.4 | 72.7 | 6.0% | 14.5 |
| B88-PBE | GGA | 996.3 | 863.8 | 112.4 | 72.6 | 6.0% | 14.6 |
| B88-LYP | GGA | 996.5 | 864.0 | 112.2 | 72.6 | 6.0% | 14.5 |
| PW86-P86 | GGA | 996.9 | 863.6 | 112.8 | 73.0 | 5.7% | 14.2 |
| PW86-PW91 | GGA | 996.5 | 863.4 | 112.7 | 72.8 | 5.8% | 14.5 |
| PW86-PBE | GGA | 996.5 | 863.3 | 112.7 | 72.8 | 5.8% | 14.5 |
| PW86-LYP | GGA | 996.7 | 863.6 | 112.5 | 72.7 | 5.9% | 14.4 |
| PBE-P86 | GGA | 996.6 | 863.8 | 112.6 | 72.9 | 5.8% | 14.3 |
| PBE-PW91 | GGA | 996.3 | 863.7 | 112.4 | 72.7 | 5.9% | 14.6 |
| PBE-LYP | GGA | 996.4 | 863.8 | 112.3 | 72.6 | 6.0% | 14.5 |
| PBE | GGA | 996.2 | 863.3 | 112.4 | 72.7 | 6.0% | 14.6 |
| PBEOP | GGA | 996.2 | 863.7 | 112.2 | 72.5 | 6.1% | 14.7 |
| BOP | GGA | 996.4 | 863.9 | 112.1 | 72.5 | 6.1% | 14.6 |
| *M11-L* | meta-GGA | *1022.6* | *862.1* | *123.9* | *75.8* | *1.2%* | *4.7* |
| *M06-L* | meta-GGA | *1005.6* | *866.1* | *116.3* | *73.8* | *4.2%* | *10.4* |
| *BR89-B94* | meta-GGA | *1003.2* | *866.8* | *114.3* | *79.4* | *4.7%* | *11.2* |
| *BR89-PK06* | meta-GGA | *1005.7* | *868.2* | *116.2* | *74.8* | *3.9%* | *9.6* |
| PBE0 | Hybrid GGA | 1002.1 | 864.6 | 114.8 | 73.8 | 4.7% | 12.0 |
| B3LYP | Hybrid GGA | 1001.2 | 865.0 | 114.2 | 73.6 | 5.0% | 12.3 |
| B97 | Hybrid GGA | 1001.1 | 864.7 | 114.2 | 73.6 | 5.0% | 12.4 |
| M05 | Hybrid meta-GGA | 1004.0 | 864.7 | 115.4 | 73.6 | 4.5% | 11.4 |
| M06 | Hybrid meta-GGA | 1005.7 | 867.0 | 115.8 | 73.9 | 4.3% | 10.2 |
| *M05-2X* | Hybrid meta-GGA | *1003.7* | *864.9* | *115.2* | *74.2* | *4.4%* | *11.3* |
| M06-2X | Hybrid meta-GGA | 1003.6 | 865.2 | 115.6 | 74.3 | 4.3% | 11.2 |

*Note*: Error measures relate to experimental values listed in the first row. Italicized rows include a change in valence electron configuration from $4s^{2}3d^{8}$ in the ground state to $4s^{1}3d^{9}$ in the core-ionized state.

[a] Root mean squared error: $100\% \times \sqrt{\frac{1}{4}\cdot\sum_{i=1}^{4}\left(\frac{x_i - x_{i,exp.}}{x_{i,exp.}}\right)^{2}}$.

[b] Mean unsigned error: $\frac{1}{4}\cdot\Sigma_{i=1}^{4}\left|\left(x_i - x_{i,exp.}\right)\right|$.

these calculations. Table 2 shows that cc-pV*n*Z calculations converge by $n = 3$ to within ±0.1 eV for M-shell (3*s* and 3*p*) CEBE values, but are not yet converged at $n = 5$ for L-shell (2*s* and 2*p*) CEBE values. The cc-pwCV*n*Z calculations do converge by $n = 3$ to within ±0.1 eV for both L-shell and M-shell CEBE values. The rate of basis set convergence is consistent between scalar relativistic and non-relativistic calculations, so the relativistic correction (taken as their difference) converges even more rapidly.

Douglas-Kroll-Hess scalar relativistic corrections to CEBE values were calculated as the difference between relativistic and non-relativistic values obtained with cc-pV*n*Z, cc-pV*n*Z-DK and cc-pwCV*n*Z, cc-pwCV*n*Z-DK basis sets. These corrections were obtained using the Hartree-Fock method and a few selected density functionals. Table 3 shows that these corrections are not very sensitive to basis set size, as the values obtained in the smallest basis sets are already converged to within ≈ ±0.1 eV. Relativistic corrections calculated with the M06-L meta-GGA density functional are similar to those calculated with the Hartree-Fock method, to within a few tenths of an eV. Relativistic corrections calculated with the BOP hybrid density functional differ slightly more from the Hartree-Fock values for the nickel atom. Still, these differences among density

**TABLE 5** Copper atom core electron binding energies in eV calculated with Δ-SCF methods and the cc-pwCVTZ basis set, including a DKH scalar relativistic correction calculated at the Hartree-Fock level

| Method | Family | Cu 2*s* | Cu 2*p* | Cu 3*s* | Cu 3*p* | RMSE[a] | MUE[b] |
|---|---|---|---|---|---|---|---|
| Experiment [28] | | 1106 | 947.0 | 128.8 | 83.0 | | |
| HF | | 1107.0 | 945.9 | 131.9 | 83.6 | 1.3% | 1.0 |
| MP2 | | 1114.2 | 950.8 | 132.0 | 84.0 | 1.4% | 4.1 |
| Slater-VWN | LSDA | 1081.2 | 943.2 | 121.1 | 79.4 | 3.8% | 9.9 |
| Slater-PZ81 | LSDA | 1081.2 | 943.3 | 121.1 | 79.4 | 3.8% | 9.9 |
| Slater-PW92 | LSDA | 1081.2 | 943.2 | 121.1 | 79.4 | 3.8% | 9.9 |
| Slater-Wigner | LSDA | 1080.3 | 942.2 | 120.4 | 78.7 | 4.3% | 10.7 |
| B88-P86 | GGA | 1083.4 | 942.8 | 121.7 | 79.5 | 3.6% | 9.3 |
| B88-PW91 | GGA | 1083.1 | 942.7 | 121.6 | 79.3 | 3.7% | 9.5 |
| B88-PBE | GGA | 1083.0 | 942.6 | 121.5 | 79.3 | 3.7% | 9.5 |
| B88-LYP | GGA | 1083.1 | 942.8 | 121.4 | 79.2 | 3.8% | 9.5 |
| PW86-P86 | GGA | 1083.4 | 942.3 | 122.1 | 79.6 | 3.5% | 9.3 |
| PW86-PW91 | GGA | 1083.1 | 942.2 | 121.9 | 79.4 | 3.6% | 9.4 |
| PW86-PBE | GGA | 1083.0 | 942.1 | 121.9 | 79.4 | 3.6% | 9.5 |
| PW86-LYP | GGA | 1083.2 | 942.3 | 121.7 | 79.3 | 3.7% | 9.5 |
| PBE-P86 | GGA | 1083.2 | 942.6 | 121.8 | 79.5 | 3.6% | 9.3 |
| PBE-PW91 | GGA | 1082.9 | 942.5 | 121.6 | 79.4 | 3.7% | 9.5 |
| PBE-LYP | GGA | 1083.0 | 942.6 | 121.4 | 79.2 | 3.8% | 9.6 |
| PBE | GGA | 1082.8 | 942.3 | 121.6 | 79.3 | 3.7% | 9.6 |
| BOP | GGA | 1083.0 | 942.7 | 121.3 | 79.1 | 3.9% | 9.6 |
| PBEOP | GGA | 1082.8 | 942.5 | 121.3 | 79.1 | 3.9% | 9.7 |
| M11-L | meta-GGA | 1109.0 | 940.7 | 135.7 | 82.9 | 2.7% | 4.2 |
| M06-L | meta-GGA | 1092.5 | 944.7 | 126.3 | 81.2 | 1.6% | 5.0 |
| BR89-B94 | meta-GGA | 1090.3 | 945.8 | 123.8 | 80.5 | 2.6% | 6.0 |
| BR89-PK06 | meta-GGA | 1092.7 | 947.0 | 125.7 | 81.6 | 1.6% | 4.4 |
| PBE0 | Hybrid GGA | 1089.0 | 943.4 | 124.4 | 80.6 | 2.4% | 6.7 |
| B3LYP | Hybrid GGA | 1088.1 | 943.8 | 123.7 | 80.4 | 2.6% | 7.1 |
| B97 | Hybrid GGA | 1088.0 | 943.6 | 123.7 | 80.3 | 2.7% | 7.2 |
| M05 | Hybrid meta-GGA | 1090.5 | 943.4 | 125.7 | 81.1 | 1.8% | 5.9 |
| M06 | Hybrid meta-GGA | 1092.3 | 945.8 | 125.9 | 81.2 | 1.7% | 4.8 |
| M05-2X | Hybrid meta-GGA | 1090.8 | 943.7 | 124.5 | 81.6 | 2.0% | 5.9 |
| M06-2X | Hybrid meta-GGA | 1090.7 | 944.0 | 124.8 | 81.7 | 1.9% | 5.8 |

*Note*: Error measures relate to experimental values listed in the first row.

[a] Root mean squared error: $100\% \times \sqrt{\frac{1}{4} \cdot \sum_{i=1}^{4} \left( \frac{x_i - x_{i,exp.}}{x_{i,exp.}} \right)^2}$.

[b] Mean unsigned error: $\frac{1}{4} \cdot \Sigma_{i=1}^{4} \left| \left( x_i - x_{i,exp.} \right) \right|$.

functionals are small. For 2*s* CEBE values, these single-configurations, scalar relativistic corrections differ by only ≈ 1 eV from available literature values based on a multi-configurational, fully relativistic treatment [17].

### 3.2 | Core electron binding energies

Core electron binding energies were calculated using the Δ-SCF approach and the cc-pwCVTZ basis set with a variety of single-configuration methods. Scalar relativistic corrections calculated at the Hartree-Fock level were added to each calculated binding energy. Some calculations for the nickel atom include a change in valence electron configuration, indicated by italics in Table 4.

Surprisingly, none of the methods tested could unambiguously improve upon the accuracy of the Hartree-Fock method. Correlation energy captured in MP2 calculations lowered the ground state energy more than those of core-ionized states, increasing all CEBE values. All methods underestimated the core electron binding energies of the nickel atom, so the MP2 method offered a modest improvement in accuracy for the nickel atom. However, the Hartree-Fock method overestimated the Cu 2*s*, 3*s*, and 3*p* CEBE values and only slightly underestimated the Cu 2*p* CEBE value, and thus outperformed MP2 predictions for the copper atom (Table 5).

Density functional methods underestimated core electron binding energies of both nickel and copper atoms. Most density functionals lowered the ground state energy less than those of core-ionized states, decreasing all predicted CEBE values. This behavior contrasts with that of the MP2 calculations, and is consistent with a reduced self-interaction error in core-ionized states relative to the ground state. The notable exception is the Minnesota meta-GGA functional M11-L, which lowered the 2*s* and 3*s* core-ionized state energies less than the ground state energy, yielding higher core electron binding energies for these states than the Hartree-Fock method. This substantially improved the accuracy of M11-L predictions for the nickel atom. It was not advantageous for the copper atom, as the Hartree-Fock method already overestimated the Cu 2*s* and 3*s* CEBE values.

Of the density functional methods, only a few meta-GGA functionals could reproduce CEBE values at a level of accuracy comparable to the Hartree-Fock method. The Minnesota meta-GGA functional M11-L performed well for both nickel and copper atoms. For the copper atom, several other meta-GGA functionals also performed well, including an older Minnesota meta-GGA functional M06-L and a combination of BR89 exchange with PK06 correlation. Hybrid meta-GGA functionals including M06 also performed well for the copper atom.

## 4 | CONCLUSIONS

Core electron binding energies have been calculated for selected, first-row transition metal atoms using standard quantum chemical methods with the Δ-SCF approach. This approach also could be applied to transition metal compounds, for which chemical shifts in photoelectron spectra are sensitive to the metal oxidation state and other aspects of the coordination environment.

The Δ-SCF approach predicts core electron binding energies by leveraging single-determinant, ground-state quantum chemical methods to calculate core-ionized state energies. For lighter atoms such as carbon and nitrogen, benchmarking studies are available in the literature to show that some density functionals can improve the accuracy of these predictions by capturing some correlation energy. Highly parameterized density functionals such as M06-L appear successful in this regard, and the SCAN functional also appears promising [5], but there is no single family of density functionals that performs well uniformly. In this context, the present study on transition metal atoms suggests that these highly accurate Δ-SCF predictions of core electron binding energies for lighter, main group atoms rely on a fortuitous cancellation of errors. More specifically, ground state densities suffer from a greater self-interaction error than core-ionized densities, but for lighter atoms the resulting error seems to be offset by an unbalanced treatment of correlation that trends in the opposite direction. While a short-range corrected functional such as those parameterized by Besley and others could rebalance the treatment of SIE for core-ionized states [7], accurate prediction of CEBE values for all elements would additionally require a balanced treatment of correlation.

The present work demonstrates that Δ-SCF calculations using density functionals systematically underestimate CEBE values for nickel and copper, rather than improving upon the accuracy of pure Hartree-Fock exchange. This could be explained by a substantial reduction in self-interaction error for core ionized states of these heavier atoms, due to their higher nuclear charge and resulting compactness of core hole densities. Calculations with the MP2 method imply that the treatment of correlation is unbalanced in the opposite direction, even leading to overestimation of core electron binding energies for the copper atom. Yet for these atoms, correlation energy differences captured by standard density functionals do not appear large enough to offset the difference in self-interaction.

Although pure Hartree-Fock exchange outperforms all density functionals, some meta-GGA functionals offer a comparable level of accuracy. The performance of the M11-L functional is comparable to that of the Hartree-Fock method for both of the selected atoms. For the copper atom, several meta-GGA functionals and even meta-GGA hybrid functionals perform comparably well. Meta-GGA functionals may therefore be useful when predicting chemical shifts in larger systems, for which they may be better suited than the Hartree-Fock method to represent changes in valence electronic structure that influence these chemical shifts. Systematic error due to imbalance in the treatment of core-ionized and ground states should be similar for closely related species, and thus cancel out when predicting chemical shifts. Therefore, accurate prediction of absolute core electron binding energies in transition metal atoms can easily justify the use of these methods to predict chemical shifts in more complex environments. Such calculations are the focus of a forthcoming manuscript that will focus on chemical shifts in closed-shell, charge-neutral complexes.

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## AUTHOR CONTRIBUTIONS

**Jason V. Jorstad:** Data curation; formal analysis; investigation; writing – original draft. **Tian Xie:** Data curation; formal analysis; investigation; validation. **Christine M. Morales:** Conceptualization; data curation; formal analysis; investigation; methodology; project administration; supervision; writing – review and editing.

## DATA AVAILABILITY STATEMENT

Data available on request from the authors.

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