Transition Metals to Heavy Elements: Morse Molecules and Beyond

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With the advent of spectroscopic methods such as resonant two-photon ionization (R2PI) spectrometry by Morse,[1] an unprecedented gauge is now available to critically evaluate existing and new theoretical methodologies. While a plethora of energetic data (i.e., dissociation energies, ionization energies, electron affinities, enthalpies) is available for early main group chemistry, including well over a thousand energies with experimental uncertainties of 1 kcal mol^{-1} or less, the availability of a broad set of high quality, low experimental uncertainty data for transition metal and heavy element chemistry has been quite limited. In fact, "transition metal chemical accuracy" (3 kcal mol^{-1}) [2] and "lanthanide chemical accuracy" (5 kcal mol^{-1}) [3] were introduced to reflect the average experimental uncertainties for some of the best enthalpies of formation for species of the lower periodic table.

R2PI, reaching experimental uncertainties of < 0.3 kJ mol^{-1} in dissociation energies, provides a route for new insight into theoretical methods for transition metal and heavy element chemistry. Using the *"Morse molecules"* – the molecules characterized by R2PI – as framework, a new variety of *ab initio* composite methods, the **super correlation consistent Composite Approach** (**super-ccCA**, or **s-ccCA**),[4] has been developed. A broad range of molecules is investigated, including those with substantial multireference character, as assessed with transition metal multireference diagnostics.[5] As well, the impact of this shift in the uncertainty scale upon a number of additional methods is considered.

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