

Abstract Submitted
for the MAR10 Meeting of
The American Physical Society

Accurate binding energies in transition-metal molecules using a position-dependent GGA+U(R) approach HEATHER KULIK, NICOLA MARZARI, DMSE MIT — Despite the importance of transition metals in a variety of biological and inorganic systems, density functional theory calculations often fail quantitatively in describing the stable intermediate electronic structures, splittings, and geometries as well as reaction barriers and geometries of transition states. We have shown how augmenting the generalized- gradient approximation (GGA) with a Hubbard U, which is obtained from a self-consistent linear response procedure, can greatly improve energetic and structural descriptions of both small, prototypical systems, such as Fe₂, and large systems like Co(II) porphyrin SAMs. However, one major shortcoming of this approach remains: we must use a calculated average of the values of Hubbard U when comparing points along a potential energy surface. We now introduce an improvement to GGA+U that incorporates variations in the value of linear-response U with changes in geometry. We show a few examples where this position-dependent GGA+U(R) approach proves particularly useful by improving binding energies and frequencies. We also present a protocol for predicting the change in U with respect to changes in coordinates, as a tool for deciding whether a standard GGA+U approach is sufficient. This approach may be directly included in structural relaxations, transition-state finding methods, and dynamics calculations.

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Date submitted: 20 Nov 2009

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