

CHEMICAL ANALYSIS OF PLANE-WAVE PAW CALCULATIONS USING PROJECTIONS TO A LOCALIZED BASIS

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The quantum chemistry of solids has tremendously profited from density-functional theory [1], notably since band structures were computed using tight-binding linear muffin-tin orbital theory in the atomic-sphere approximation [2], for obvious reasons. Nowadays, calculations using plane-wave basis sets have become increasingly popular as these methods are believed to offer other computational benefits, e.g., accurate forces and the absence of any basis-set bias [1]. By using the projector-augmented wave (PAW) approach [3], reliable plane-wave electronic structures are easily available from first principles while the computational costs are only moderate. Nonetheless, it is quite challenging to fully *understand* the often complex results and, consequently, simple yet powerful chemical concepts such as COOP [4] originating from extended Hückel and COHP [5] from LMTO theory are truly needed. Due to the lack of basis locality, the latter quantities were so far unavailable within the plane-wave based approaches. We have recently shown, however, that local information of the above kind can indeed be reconstructed from plane waves yielding a projected COHP [6] but the quality of the chemical analysis depends crucially on the very projection for reconstructing the density and Hamiltonian matrices. As conventional methods give rather poor results, a new and analytical framework to transfer PAW functions to a localized basis built from Slater-type orbitals (STO) has been developed in order to eventually yield a proper bonding analysis [7]. We follow the chemist's LCAO-CO route and model the PAW part using linear combinations of contracted Slater functions [8], which have proven to be an adequate choice, and hereby regain the coefficient matrix to yield the desired local quantities. Because an STO basis is not innately orthogonal, the theory to reconstruct the Hamiltonian and the projected COHP [6] originally formulated for orthogonal basis sets had to be generalized by removing the orthogonality restraint [7]. By doing so, this method straightforwardly yields the projected analogues of the density-of-states (DOS), COOP and COHP. In addition, the projected local DOS provide an improvement over more traditional projections with respect to charge conservation. To actually enable chemical-bonding analyses, we present a computer program that calculates all aforementioned quantities based on self-consistent PAW results.

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