# Electronic Supplementary Information

## Solid State Adaptive Natural Density Partitioning: A Tool for Deciphering Multi-center Bonding in Periodic Systems[†]

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**Appendix A. AO-PW Projection Developments**

AdNDP requires the density matrix in an atom-centered basis. However, delocalized plane wave basis sets are ubiquitous in solid state calculations. To interface SSAdNDP with these widely used basis sets, we use a projection algorithm, which maximally represents the plane wave orbitals, $|\psi_\alpha(r)\rangle$, in a Guassian-type atom-centered basis, $|\phi_\mu(r)\rangle$, giving the projected orbitals, $|\chi_\alpha(r)\rangle = \sum_\mu b_{\alpha,\mu} |\phi_\mu(r)\rangle$. The projection algorithm used is described in detail in Ref. 11, with slight modifications.

The primary difference in the implementation of the projection algorithm is in how the pseudopotential is accounted for. In this study projector augmented-wave pseudopotentials were used.[38] As described in Ref. 11, this necessitates the calculation of overlap integrals between the AO basis functions and augmenter functions, $\Delta w_i(r) = Y^{l_i m_i} R(|r - r_i|)$, located at each atomic center, $r_i$. In instances where the AO and augmenter functions were centered on different atoms a first order Taylor expansion was used to represent the AO function, centered at $r_\mu$, around the center where the augmenter function is located. Here we have extended this expansion to second order,

$$\phi_\mu(r - r_\mu - s) \square\ \phi_\mu(r_i - r_\mu - s) + \nabla\phi_\mu(r_i - r_\mu - s)\square(r - r_i) + $$
$$\frac{1}{2}[\nabla(\nabla\phi)(r_i - r_\mu - s)\square(r - r_i)] + \sum_{x_1 > x_2} \frac{\partial^2}{\partial x_1 \partial x_2}\phi_\mu(r_i - r_\mu - s)(r_{x_1} - r_{i,x_1})(r_{x_2} - r_{i,x_2})\ ,$$

where s denotes the unit cell $\phi_\mu(r)$ is located in relative to the central unit cell, 0. This Taylor expansion is equivalent to an expansion of the AO function into cartesian spherical harmonics up to second order ($l$=0,1,2) around the augmenter center, which allows for a separation of the overlap integral into angular and radial components. Note that due to the use of cartesian spherical harmonics, there are six second order terms ($x^2$, $y^2$, $z^2$, $xy$, $xz$, $yz$), the first three of which overlap with both $s$- and $d$-type spherical harmonics.

While the plane wave basis is considered mostly complete, which atomic orbital basis is appropriate for a particular solid is unclear. The quality of a particular basis set in representing the plane wave orbitals can be quantified by taking the difference of the norm of the projected band and the norm of the original plane wave orbital, $\langle \psi_\alpha(r) | \psi_\alpha(r) \rangle - \langle \chi_\alpha(r) | \chi_\alpha(r) \rangle$. In general this value is rigorously limited within the range of 0 to 1, corresponding to a full representation of the band in the AO basis and total failure of the AO basis, respectively. However, when the Taylor series approximation is used in the projection, it becomes possible for the projected orbitals to have a norm larger than the original occupied orbitals, corresponding to more density. As long as the approximation is appropriate, this error is minimal. It was previously assumed that off-site overlap with $d$-type PAWs could be approximated as zero due to these functions' oscillatory nature. However, the extension to a second order Taylor expansion and therefore inclusion of explicit $d$-type overlap has been seen to be necessary to keep the error below one percent per band.