Exploring quantum transport and chemical bonding using *ab initio* quasiatomic orbitals

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We have developed an efficient and robust method[1] to transform Bloch wavefunctions obtained from density-functional theory calculations into a set of localized nonorthogonal quasiatomic orbitals, which are maximally similar to the Bloch subspace spanned by atomic orbitals. Accurate tight-binding band structure, Fermi surface, and Mulliken and Löwdin charge analysis can be carried out easily. Here we show three important applications of quasiatomic orbitals. First, by combining the *ab initio* tight-binding Hamiltonian and Green's function method[2] we can efficiently study phase-coherent quantum transport within the Landauer formalism while keeping accuracy at the level of planewave density-functional theory. Second, the localized quasiatomic orbitals constructed from extended Bloch wavefunctions provide us a convenient bridge to construct natural bond orbitals[3] and maximum hybridization orbitals[4] to study chemical bonding in complex materials. Finally, we demonstrate that decomposition of polarization changes under external perturbation into quasiatomic orbital basis can help understand the microscopic mechanism of polarization changes.

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