A self-consistent full-potential NMTO method and code

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N^{th}-order muffin-tin orbitals (NMTOs) constitute a class of minimal one-electron basis sets. Such a set provides the exact solutions of Schrödinger's equation for an overlapping MT (OMT) potential at N+1 chosen energies, and interpolates smoothly between those energies. An NMTO set may be chosen to pick particular bands. Its envelope functions are a set of screened spherical waves (SSWs), i.e. solutions of the wave equation with the boundary conditions that a SSW at site $\boldsymbol{R}$ and with angular-momentum character *lm* vanishes at non-touching, so-called *hard spheres* in all *other* $\boldsymbol{R}lm$-channels. Orthonormalized NMTOs are localized, atom-centered Wannier functions generated directly in real space with Green-function multiple-scattering techniques and without projection from band states. Depending on which and how many bands, i.e. which and how many NMTOs are included in the basis set (the so-called the degree of downfolding), the shape of these orbitals change from atomic-like for large sets to bond-like for small sets. The respective sets are useful for including Coulomb correlations and visualizing covalency. It is possible to generate NMTO sets which span merely the occupied bands, even for metals. The NMTO method provides tight-binding Hamiltonians and single-particle orbitals.

However, NMTOs are complicated objects. Unlike plane waves, Gaussians, and LMTOs in the ASA, *products* of NMTOs are not simple functions for which Poisson's equation is trivially solved, because in addition to an ASA-like sum of spherical harmonics times radial functions, which vanish outside the OMTs, they are products of SSWs, which vanish inside the hard spheres. Since these SSW products are difficult to treat, NMTOs have so-far only been used to solve Schrödinger's equation for OMT potentials obtained self-consistently with some other method.

This, we have now remedied by developing Methfessel's method of interpolating a smooth function across the hard-sphere interstitial by fitting the values and first 3 radial derivatives of its spherical-harmonics projections on all hard spheres to a *sum* of SSWs. for which it is trivial to solve Poisson's equation. In detail, we first linear combine the set of SSWs with different $\boldsymbol{R}lm$s and 4 different decay constants, λ_i, into a set of structural "value-and-derivative functions" having the property that the $\boldsymbol{R}'l'm'i'$–projection of the $\boldsymbol{R}lmi$ function is $\delta_{\boldsymbol{R}lmi,\boldsymbol{R}'l'm'i'}$. These functions are localized and solving Poisson's equation for them is trivial.

Our new self-consistent full-potential code includes least-squares fitting of the full-potential output to the OMT form which is used to define the NMTO basis for the next iteration. The one-electron Hamiltonian is given by the kink matrix, a correction for potential overlap beyond 1$^{\text{st}}$ order, and the full-potential. The full charge density and the total energy are computed by use of the above-mentioned value-and-derivative functions. As an example, we compute the elastic constants of silicon and compare with other LDA results and experiments.