Maximum Overlap Method (MOM) in the solid state

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ABSTRACT

The maximum overlap method, unlike the Aufbau principle, during the SCF iterations tries to maximize the overlap between the occupied orbitals with those of the preceding iteration or of a reference state. This procedure leads the SCF towards excited state solutions instead of ground state ones, or can be useful in order to stabilize the ground state solution preventing the intrusion of unphysical states in the density matrix.
In fact, it is well known that starting from the time independent Schrödinger wave equation, we can generalize the problem as an eigenvalue problem in each k point of the reciprocal space Brillouin zone:

$$F(k)C^{new}(k) = S(k)C^{new}(k)\varepsilon$$

with S as overlap matrix, is then solved to obtain a new MO coefficient matrix C^{new} and orbital energies ε [1,2].
Usually with the Aufbau protocol, the occupation of orbitals starts with the lowest orbital energies ε. On the contrary, the MOM method determines the new orbitals occupation by looking at those orbitals whose have the greatest overlap with the old occupied ones:

$$O(k) = \left(C^{old}(k)\right)^{\dagger} S(k)C^{new}(k)$$

The projection of the jth new orbital onto the old occupied space is expressed by:

$$p_j(k) = \sum_{i}^{n} O_{ij}(k) = \sum_{v}^{N}\left[\sum_{\mu}^{N}\left(\sum_{i}^{n} C_{i\mu}^{old}(k)\right)^{\dagger} S_{\mu v}(k)C_{vj}^{new}(k)\right]$$

where Oij is the overlap between the ith old orbital and the jth new orbital. The occupation is finally determined by the largest projections p_j.
Promoting an electron from an occupied to a virtual orbital is then a sufficient guess to start an SCF calculation with MOM. In fact, the algorithm will keep the excited configuration.
We implemented the MOM algorithm in the CRYSTAL code [3], a program developed by University of Turin for the quantum chemical study of crystalline solid that adopts a local basis set of Gaussian functions centered on atoms.

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