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Computing the density of states (DOS) and its various projections.

The density matrix in AO basis:

$$P_{ab} = \left(COC^T\right)_{ab} = \sum_k C_{ak} O_{kk} C_{bk} \; . \tag{1}$$

The charge density matrix (population) is:

$$D = PS \; . \tag{2}$$

The diagonal elements of D, D_{ii}, give the population on the orbital i – this population comes from states of different energy.

$$D_{ii} = (PS)_{ii} = \sum_j P_{ij} S_{ji} = \sum_j \sum_k C_{ik} O_{kk} C_{jk} S_{ji} = \sum_k O_{kk} \sum_j C_{ik} C_{jk} S_{ji} = \\ = \sum_k n(\varepsilon_k) DOS_i(\varepsilon_k) \tag{3}$$

where $DOS_i(\varepsilon_k) = \sum_j C_{ik} C_{jk} S_{ji}$ is the contribution of the AO i to the density of states at energy ε_k. This is an orbital-resolved DOS.

From the additivity of the charge density matrix, we can derive that:

a) for orbitals of given type α (orbital-type-resolved DOS):

$$DOS_\alpha(\varepsilon_k) = \sum_{i \in \alpha} DOS_i(\varepsilon_k) = \sum_{i \in \alpha} \sum_j C_{ik} C_{jk} S_{ji} \; . \tag{4}$$

b) for orbitals on given atom A (atomic-type-resolved DOS):

$$DOS_A(\varepsilon_k) = \sum_{i \in A} DOS_i(\varepsilon_k) = \sum_{i \in A} \sum_j C_{ik} C_{jk} S_{ji} \; . \tag{5}$$

c) for orbitals of given type α centered on given atom A (type-and-atomic-resolved DOS):

$$DOS_{\alpha A}(\varepsilon_k) = \sum_{i \in \alpha A} DOS_i(\varepsilon_k) = \sum_{i \in \alpha A} \sum_j C_{ik} C_{jk} S_{ji} \; . \tag{6}$$

Some additivity rules:

1) $DOS_A(\varepsilon_k) = \sum_{\alpha \in A} DOS_{\alpha A}(\varepsilon_k)$ sum of DOS of states of all type with states centered on a given atom gives the atomic-resolved DOS for given atom

2) $DOS_\alpha(\varepsilon_k) = \sum_{A \in \alpha} DOS_{\alpha A}(\varepsilon_k)$ sum of type-and-atomic-resolved DOSs over all atoms gives DOS resolved in the state type

3) $DOS(\varepsilon_k) = \sum_\alpha DOS_\alpha(\varepsilon_k) = \sum_A DOS_A(\varepsilon_k) = \sum_{\alpha A} DOS_{\alpha A}(\varepsilon_k) = \sum_i DOS_i(\varepsilon_k)$ total DOS via DOSs of different resolution type

Form $tr(PS) = N$ we also get:

$\sum_{k,i} n(\varepsilon_k) DOS_i(\varepsilon_k) = N$ total number of electrons, also this can be applied to resolve number of electrons of given type (type of orbital, atom localization, both).