Density fitting and multipole approximations in periodic local quantum chemical methods: Using physical principles in tensor decompositions

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Quantum chemistry aims at first-principle predictions of molecular or crystalline system properties, such as equilibrium structures, relative stabilities, reaction energies, frequencies of atomic vibrations, etc. Most of the quantum chemical approaches address the Schrödinger equation, involving nucleus-nucleus, nucleus-electron and electron-electron Coulomb interactions, within the Born-Oppenheimer approximation, which separates the nuclear and electron motions.
In order to maintain the antisymmetry of the many-electron wavefunction, it is represented in the basis of Slater determinants, i.e. determinants constructed from one-electron functions (orbitals). The formalism for solving the electronic Schrödinger equation within such a basis reduces to systems of equations with the coefficients constructed from various integrals of one-electron orbitals. The key quantities in this formalism are the 4-index two-electron Coulomb integral:

$$K_{ab}^{ij} \equiv (ia|jb) = \int d\mathbf{r}_1 \; \phi_i(\mathbf{r}_1)\phi_a(\mathbf{r}_1) \int d\mathbf{r}_2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\phi_j(\mathbf{r}_2)\phi_b(\mathbf{r}_2), \tag{1}$$

where $\mathbf{r}$ is a position vector and $\phi_x(\mathbf{r})$ are localized orbitals. Computation of these integrals and their contractions becomes considerably more efficient if the tensor decomposition of the type

$$(ia|jb) \approx \sum_P B_P^{ia} B_P^{jb} \tag{2}$$

is used. This approach can be furthermore substantially facilitated by taking into account the physical aspects of the problem:

- The structure of the integral to be decomposed
- The Coulomb integral kernel
- The locality of the orbitals
- The possibility to assign the index P also to local functions.
- Translational symmetry (in periodic systems)

The implication of these properties in the tensor decompositions (2) is analyzed in detail.