Invertible mappings between operators and their finite-dimensional matrix representations

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Basis sets of one-electron functions that form linearly independent products (LIPs) possess a number of remarkable properties which were first pointed out by Harriman. In particular, LIP basis sets make it possible to reconstruct multiplicative ("local") potentials from their matrix representations in a rigorous and unambiguous manner. Although standard basis sets of quantum chemistry almost never form LIPs, occupied canonical self-consistent field orbitals of small atoms and molecules routinely do so. Using these principles we recover various parts of the Kohn–Sham Hamiltonian and Fock operators from respective matrices and obtain new insights into the Kohn–Sham inversion problem, kinetic potential, and performance of density-functional approximations within finite basis sets.