Exact Atomic-Pair-Interaction Representations of Molecular Hamiltonian Matrices[1] P.W. LANGHOFF, M. BEN-NUN, K. ROLLIN, UCSD, La Jolla, J.D. MILLS, J.A. BOATZ, AFRL, Edwards AFB, R.J. HINDE, UT, Knoxville, G.A. GALLUP, UN, Lincoln — Progress is reported in the implementation of a novel theoretical method for ab initio calculations of molecular potential energy surfaces. The theory is based on use of (Eisenschitz-London) products of atomic spectral eigenstates in the absence of explicit aggregate antisymmetry. An exact atomic-pair-interaction theorem is devised for such atomic spectral product Hamiltonian matrices. It is shown that atomic pair antisymmetry, which is enforced subsequent to matrix construction, is sufficient to exclude the non-Pauli solutions of the Schrödinger equation spanned by the atomic product representation. Aspects of a computer code suite devised to perform such calculations are described, including calculations of many-electron atomic eigenstates and pairwise atomic interactions employing valence bond methods in even-tempered Slater-orbital basis sets, enforcement of atomic pairwise antisymmetry employing diatomic metric matrices, use of Wigner rotation matrices for the angular degrees of freedom of atomic interaction matrices, and spin re-coupling formalism. Illustrative small molecule and cluster applications provide potential energy surfaces in agreement with fully antisymmetric valence-bond results, including avoided crossings and conical intersections in excited states.

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