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Spectral-product representations of atomic and molecular Hamiltonians[1] P.W. LANGHOFF, UCSD, R.J. HINDE, UTK, J.D. MILLS, J.A. BOATZ, AFRL/PRS — An alternative approach to *ab initio* computational studies of the electronic structure of matter is described. Antisymmetry restrictions are enforced subsequent to construction of the Hamiltonian matrix for an atom or molecule in an orthonormal spectral-product basis. Transformation to a permutation-symmetry representation obtained from the eigenstates of the aggregate electron antisymmetrizer enforces the requirements of the Pauli principle, and eliminates the unphysical (non-Pauli) states spanned by the product basis. Results identical with conventional use of prior basis-state antisymmetry are obtained in applications to many-electrons atoms. For polyatomic molecules, the development accommodates incorporation of fragment information in the form of Hermitian matrix representatives of atomic and diatomic operators which include the non-local effects of overall electron antisymmetry, providing a new exact atomic-pair representation of polyatomic Hamiltonian matrices. Illustrative applications to the well-known low-lying doublet and quartet states in the H_3 molecule demonstrate that the eigensurfaces of the antisymmetrizer can anticipate the structures of the more familiar energy surfaces, including seams of conical intersection. The calculated energy surfaces are found to be in good agreement with corresponding accurate values obtained from valence-bond and higher-level computational procedures.

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