On the Computational Aspects of the Scalar Hermitian Product versus the Complex Product for Complex Wave Functions of Temporary Anion States: Electron Densities and Fukui Functions of Be^-, Mg and Ca^-

Robert C. Morrison
Department of Chemistry
East Carolina University
Greenville, North Carolina 27858

Abstract

The impetus for using the complex product (f | g) rather than the scalar Hermitian product <f | g> when examining temporary anion states is the non-Hermitian nature of the Hamiltonian obtained by complex rotation of the Hamiltonian operator. For example the Helmann-Feyman theorem and the virial theorem hold when using the complex product, but not when using the scalar Hermitian product. And generally for the Hamiltonian eigenfunctions $< \Psi_K^{hp} | \Psi_L^{hp} > \neq 0$ for K ≠ L, whereas $(\Psi_K^{cp} | \Psi_L^{cp}) = 0$ for K≠L. Some properties hold for both scalar products. For example $< \Psi_K^{hp} | \hat{H} | \Psi_K^{hp} > = (\Psi_K^{cp} | \hat{H} | \Psi_K^{cp}) = E_K$, where Ψ_K^{hp} is the Kth eigenfunction normalized using the scalar Hermitian product and Ψ_K^{cp} is the eigenfunction normalized using the complex product; the two eigenfunctions only differ by normalization constants.
Temporary anion states have been examined for Be^-, Mg^-, and Ca^- using the method of complex rotation of the Hamiltonian, which produces configuration-based Hamiltonian matrices that are complex symmetric. Computational comparisons are made between the scalar Hermitian product and the complex product for calculating electron densities and Fukui functions. The Pauli principle is not satisfied when using the complex product for the real first-order reduced density matrix. The scalar Hermitian product may be preferred for calculating certain real properties.

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