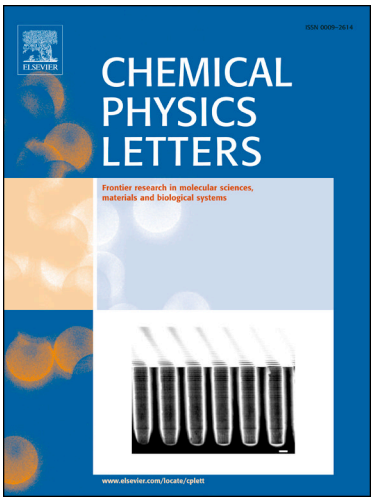

Research paper

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Efficient Evaluation of Poly-Electron Populations in Natural Bond Orbital Analysis

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Abstract

We show how a simple natural orbital-based modification of Karafiloglou's poly-electron population analysis (PEPA) [generalizing conventional one-electron natural population analysis (NPA)] allows efficient numerical evaluation of Born probabilities (populations) for an unlimited variety of localized electronic excitation patterns. The computational advantages are illustrated by simple numerical applications to CH_3NH_2 and benzene in the framework of natural bond orbital (NBO)-based "NPEPA" keyword implementation in the forthcoming *NBO 7.0* program.

Introduction

In an extended series of works, Karafiloglou and co-workers [1] have demonstrated the conceptual usefulness of "poly-electron population analysis" (PEPA) that generalizes conventional orbital populations as provided, e.g., by natural population analysis (NPA) [2]. In Karafiloglou's formulation, a specific population (or "probability of occupancy") can be assigned not only to individual localized orbitals (LOs), such as natural atomic orbitals (NAOs), natural hybrid orbitals (NHOs), or natural bond orbitals (NBOs) [3], but also to general electron-hole (*e*/*h*) excitation patterns of chemical interest. In the present work we focus on the "natural" NAO/NBO-based (NPEPA) algorithms that are implemented in the forthcoming *NBO 7.0* program version [4].

Each *e*/*h* pattern of NPEPA analysis specifies a particular combination of occupied ("electron") and vacant ("hole") spin-orbitals that may (or may not) occur in Slater-determinantal contributions to the total wavefunction Ψ. As usual, the associated "Born probability" $P(e/h)$ of such contributions is evaluated by summing the squared coefficients of all determinants exhibiting the desired pattern. For example, if the desired *e*/*h* patterns are expressed in terms of NBOs, each NBO occupancy pattern can be viewed as a distinct "resonance structure" whose Born probability quantifies the "weighting" of the bonding pattern in Ψ, thereby providing interesting comparisons with corresponding natural resonance theory (NRT) [5] weightings. If instead the analysis of Ψ is posed in terms of NAOs, the specific NAO patterns might correspond to the 2-center/2-electron (2c/2e) "covalent" or "ionic" contributions of classical Heitler-London valence-bond (VB) theory [6], thereby providing interesting comparisons with alternative assessments of VB-character in modern wavefunctions [7]. Many other questions involving deeper details of