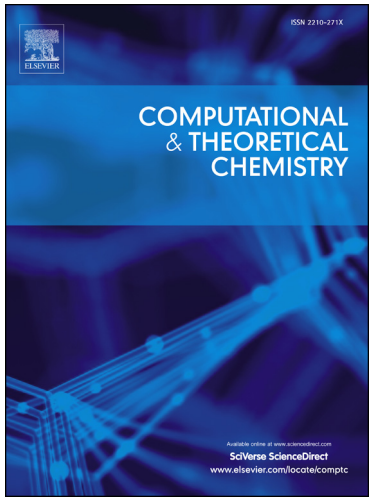

Non-Born-Oppenheimer nuclear and electronic densities for a three-particle Hooke-Coulomb model

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Non-Born-Oppenheimer nuclear and electronic densities for a three-particle Hooke-Coulomb model

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Abstract

Non-Born-Oppenheimer, nBO, one-particle nuclear and electron densities for a Hooke-Coulomb model of a three-body system are presented. These densities are obtained using exact closed-form analytic solutions to this problem as well as variational solutions. Moreover, the densities are calculated using different reference points, such as the global center of mass [**cm**], the geometric centers between both identical [**gc12**] and non-identical particles [**cm13**], and the location of the non-identical particle [**p3**]. It is shown that the topology of these nBO densities depends upon the choice of the reference points. This result is in turn used to argue that in a nBO regime the topological properties of the one-particle density cannot be univocally correlated with molecular structure, in the way it is done for the Born-Oppenheimer approximation.

Keywords: Non-Born-Oppenheimer, Hooke-Coulomb model, one-particle densities

1. Introduction

The Born-Oppenheimer, BO, approximation has been, without any doubt, a fundamental concept underlying the development of quantum-mechanical approaches to the electronic structure of molecular and crystalline systems. However, the BO approximation breaks down for many systems and processes of chemical and physical interest (see, for example, Refs. [1–8]).

Thus, in sight of this breakdown of the BO approximation and bearing in mind that some important chemical and physical phenomena occurring at the atomic level strongly depend on nuclear quantum effects, recent efforts in the field of quantum theory have been directed toward the development of methods based on a non-Born-Oppenheimer, nBO, regime [2, 9–24]. In the particular case of chemistry, the attention placed on nBO treatments has reopened the debate of whether molecular structure, a basic concept in chemistry, [25] can be derived from wave functions that include the behavior of non-clamped nuclei.[22, 26–31]

The problem is that the average distances and angles obtained from nBO wave functions generally are not sufficient to extract from them molecular structure.[32, 33] However, let us mention that as shown in recent work of Mátyus *et al.*[31] the triangular structure of the H_2D^+ ion can be retrieved from the angular density corresponding to a highly accurate nBO variational wave function.

In the context of Bader's Quantum Theory

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