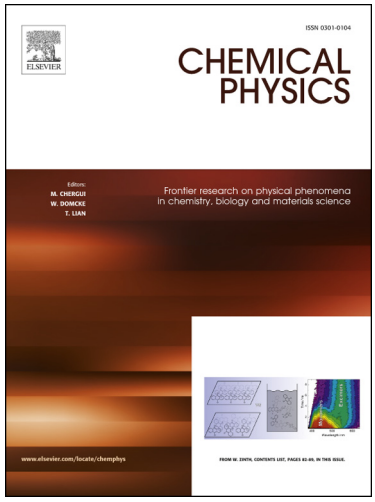

A Canonical Approach to Forces in Molecules

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A Canonical Approach to Forces in Molecules

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Abstract

In previous studies, we introduced a generalized formulation for canonical transformations and spectra to investigate the concept of canonical potentials strictly within the Born-Oppenheimer approximation. Data for the most accurate available ground electronic state pairwise intramolecular potentials in H_2^+, H_2, HeH^+, and LiH were used to rigorously establish such conclusions. Now, a canonical transformation is derived for the molecular force, $F(R)$, with H_2^+ as molecular reference. These transformations are demonstrated to be inherently canonical to high accuracy but distinctly different from those corresponding to the respective potentials of H_2, HeH^+, and LiH. In this paper, we establish the canonical nature of the molecular force which is key to fundamental generalization of canonical approaches to molecular bonding. As further examples Mg_2, benzene dimer and to water dimer are also considered within the radial limit as applications of the current methodology.

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