On the Breakdown of Born-Oppenheimer Separation in Electron Transfer Reactions: An Electron-Nuclear Dynamics Assessment.

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The Born-Oppenheimer separation is one of the cornerstones of modern electronic structure methods and has more recently been employed in the dynamics studies of a wide class of chemical reactions as direct dynamics or Born-Oppenheimer molecular dynamics (BOMD) methods. In this separation the electronic motion is uncoupled from the nuclei motion, which usually gives a good description of well defined molecular structures. However, it has been shown that the electron-nuclear couplings are needed to properly describe the differential cross sections for electron transfer in H^+ + H collisions [1]. These analyses were performed with the electron-nuclear dynamic (END) formalism as implemented in the ENDyne program at simplest level END-1 [2]. In the END formalism the electron-nuclear couplings are explicitly considered in the dynamical evolution of the molecular system. The ENDyne program allows the neglect of these couplings resulting in uncoupled equations of motion for electrons and nuclei. Thus, comparisons between END-1 calculations with and without the electron-nuclear couplings can yield direct and quantitative evidence for the breakdown of Born-Oppenheimer separation. These comparisons have been performed for the collision of C^{3+}, O^{3+} or Si^{3+} with H at several energies. It is shown [3] that upon inclusion of the electron-nuclear couplings the calculated total charge-transfer cross sections for electron transfer are in excellent agreement with the experimental ones within a wide range of energy [0.04 – 10 keV]. However, when these couplings are neglected, that is, when the Born-Oppenheimer approximation is performed, the calculated cross sections are completely unreliable and the disagreements with the experimental data occur at any collision energy. So, this provides direct evidence that not only for differential cross sections involving one-electron system, but also for the total charge-transfer cross sections in many-electrons systems the inclusion of the electron-nuclear couplings is necessary to obtain results comparable to the observed ones.

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References

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