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Beyond Born-Oppenheimer Theories: Diabatic PESs for Spectroscopic & Scattering Processes

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The formulation of beyond Born-Oppenheimer (BO) approach for two/three state sub-Hilbert space is briefly presented from first principle for the construction of diabatic potential energy surfaces (PESs) both for spectroscopic and scattering processes. We calculate adiabatic PESs and Non-Adiabatic Coupling Terms (NACTs) for the excited electronic states ($2^2E'$ and $1^2A_1'$) of alkali trimers[1,2] (Na_3 and K_3), the ground (X^2A_1) and the first excited state (A^2B_2) of NO_2[3,4], and the three lowest electronic singlet states ($1^1A'$, $2^1A'$ and $3^1A'$) of H_3^+ system[5], where both Jahn-Teller (JT) and Renner-Teller (RT) types of conical intersections (CIs) are identified. The collapse of CIs in alkali trimers at D_{3h} symmetry point and semi-circular CI seam (rather than a CI point) between the ground and first excited states of H_3^+ system are new interesting observations. While performing Adiabatic to Diabatic Transformation (ADT), the NACTs are adapted with molecular symmetry (MS) whenever necessary to assign their Irreducible Representations in order to construct totally symmetric diabatic (nuclear) Hamiltonian. The nuclear dynamics is performed on the diabatic PESs of Na_3 and NO_2 to calculate the photoelectron spectrum, which matches quite well with the experimentally measured ones.[6,7] Moreover, we carry out reactive scattering dynamics[8-11] on the adiabatic and diabatic surfaces[5] for H_3^+ system in hyperspherical coordinates for total angular momentum zero and non-zero situation to reproduce experimental cross sections and rate coefficients for reactive non-charge and charge transfer processes.[12,13]

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