DOCTORAL THESIS

Simulating electronic-structure properties of atomic clusters by Ab-initio calculations, and inter-nuclear quantum-statistical effects of molecules from an integration-free path-integral method

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Abstract

In this dissertation, we have employed some well-established electronic-structure methods [e.g., density functional theory (DFT) and time-dependent DFT (TD-DFT)] to investigate the potential energy surfaces for $2s \rightarrow 2p$ excitation of beryllium atomic clusters, attempting to provide direct computational support for the mechanism of a newly invented laser spectroscopy. The computing time of single-point energy calculations for a series of beryllium clusters from using TD-DFT has been compared with that from a higher-level coupled-cluster method, in order to demonstrate the computational practicality of TD-DFT methods. Meanwhile, to benchmark the accuracy of TD-DFT methods, the state properties such as the equilibrium inter-atomic distance and dissociation energy of beryllium clusters calculated by us are compared with experimental results and other computational values where available. Furthermore, we have defined the fork intersections to characterize the position where the excited states can be treated as degenerate.

Moreover, to shed some light on the reaction mechanism of a Diels-Alder reaction between isoprene and maleic anhydride, we have investigated the kinetic isotope effects (KIE) of the reaction. To further include inter-nuclear quantum-statistical effects (i.e., the quantum tunneling effect and anharmonicity), an automated integration-free path-integral (AIF-PI) method developed by our group in recent years based on Kleinert's variational perturbation theory has been used. The KIE values produced by the AIF-PI method can be used to clearly distinguish between the two isomeric transition-state structures, and determine the actual rate-limiting transition state. By virtue of the AIF-PI method, we have also analyzed the quantum tunneling effects and anharmonicity separately, which are excluded in conventional Bigeleisen equation. Furthermore, the influence of different numbers of quantized nuclei on the

KIE values using base-catalyzed RNA 2'-O-transphosphorylation models as examples are explored, by systematically increasing the number of quantized nuclei from 1 to 16 (fully quantized).

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