WAVE PACKET CORRELATION APPROACH TO REACTIVE SCATTERING

ABSTRACT

by

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Calculation of reaction rates lies in the very core of theoretical chemistry, since they define the significance of chemical processes. Reaction rates depend strongly, up to orders of magnitude, on the temperature of a reactive system, but there is a universal quantity for a specific reaction – the reaction probability. It yields the reaction rate for any temperature, when averaged over the energy distribution of reagents. However, an exact quantum-mechanical calculation of the reaction probability is extremely difficult: at present, state-of-the-art calculations are carried out for just a few four-atom systems.

The theoretical assessment of reaction probabilities depends on three key components: the availability and the accuracy of a potential electronic surface, the theoretical formulation of the reactive scattering problem and methods of numerical implementation. The latter two of these components are the subject of this work. An application and modification of the semiclassical method of Herman and Kluk, which is a promising alternative to the exact quantum-mechanical methods, to the calculation of the reaction probability for the collinear hydrogen exchange reaction are presented. Another aspect of this work is a derivation of analytical expressions for the reaction probability based on wave-packet dynamics. Example applications of our new expressions are presented for a test one-dimensional problem and for the collinear hydrogen-exchange reaction, using both quantum-mechanical and semiclassical propagation methods.