Transforming high-dimensional potential energy surfaces into sum-of-products form using Monte-Carlo methods

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Abstract

We present a novel method for transforming potential energy surfaces into a sum-of-products form based on Monte-Carlo sampling: Monte-Carlo Potfit. The method is based on the traditional potfit, but largely reduces the numerical effort by avoiding complete integrals. Instead Monte-Carlo integrals are used. This allows a treatment of surfaces of up to 12-15 degrees of freedom. Importance sampling is introduced streight forwardly such that relevant regions of the potential can be treated with increased accuracy. We show the power of the method by transforming a 15D potential of the protonated water dimer (Zundel cation) in a sum-of-products form and calculating the ground and lowest vibrationally excited states.

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