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标题: Application of Heisenberg's S Matrix Program to the Angular Scattering of the H + D-2(v(i)=0, j(i)=0) -> HD(v(f)=3, j(f)=0) + D Reaction: Piecewise S Matrix Elements Using Linear, Quadratic, Step-Function, and Top-Hat Parametrizations
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摘要: A previous paper by Shan and Connor (Phys. Chem Chem Phys. 2011, 13, 8392) reported the Surprising result that four simple parametrized S Matrices can reproduce the forward-angle glory scattering of the H + D-2(v(i)=0,j(i)=0) -> HD(v(f)=3,j(f)=0) + D reaction, whose differential cross section (DCS) had been computed in a state-of-the-art scattering calculation for a state-of-the-art potential energy surface. Here, v and j are vibrational and rotational quantum numbers, respectively, and the translational energy is 1.81 eV. This paper asks the question Can we replace the analytic functions (of class C-omega) used by Shan-Connor. with simpler mathematical functions and still reproduce the forward-angle glory scattering?. We first construct S matrix elements (of class C-omega) using a quadratic phase and a piecewise-continuous pre-exponential factor consisting of three pieces. Two of the pieces are constants, with one taking the value N (a real normalization constant) at small-values of the total angular momentum number, J; the other piece has the value 0 at large J. These two pieces are joined at intermediate values of J by either a straight line, giving rise to the linear parametrization (denoted pram L), or a quadratic curve, which defines the quadratic parametrization (param Q). We find that both param L and param Q can reproduce the glory scattering for center-of-mass reactive scattering angles, theta(R) less than or similar to 30 degrees. Second, we use a piecewise-discontinuous pre-exponential factor and a quadratic phase, giving rise to a step-function parametrization (param SF) and a top-hat parametrization (param TH). We find that both param. SF and param TH can reproduce the forward-angle scattering, even though these class C-1 parametrizations are usually considered too simplistic to be useful for calculations of DCSs. We find that an ultrasimplistic param THz, which is param TH with a phase of zero, can also reproduce the glory scattering at forward angles. The S matrix elements for param THz are real and consist of five nonzero equal values, given by (S) over tilde (J) = 0.02266, for the window, J = 21(1)25. Param THz is sufficiently simple that we can derive closed forms for the partial wave scattering amplitude, f(theta(R)), and the near side (N) and far side (F) subamplitudes. We show that window representations, f(theta(R)) provide important insights into the range of J values that contribute to the reaction dynamics. Other theoretical techniques used are NF theory for the analysis ofDCSs and full and NF local angular momentum theory, in both cases including up to three resummations of f(theta(R)) before making the NF decomposition. Finally, we investigate the accuracy of various semiclassical glory theories for the DCS of Param L By varying one phase parameter for param L, we show that the uniform semiclassical approximation is accurate from theta(R) = 0 degrees to close to theta(R) = 18 degrees. Our approach is an example of a "weak" form of Heisenberg's S matrix program, which does not Use a potential energy surface(s); rather it focuses on the properties of the S matrix. Our Method is easy to apply to DCSs from experimental measurements or from computer simulations.

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