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This Week's Citation Classic

Secrest D & Johnson B R. Exact quantum-mechanical calculation of a collinear collision of a particle with a harmonic oscillator.
J. Chem. Phys. 45:4556-70, 1966.
[Dept. Chem. and Chem. Eng., and Dept. Phys., Univ. Illinois, Urbana, IL]

Exact quantum-mechanical calculations of the transition probabilities for the collinear collision of an atom with a diatomic molecule are reported. The molecule is treated as a harmonic oscillator and a range of interaction potentials from very hard to very soft are considered. [The *SCI*® indicates that this paper has been cited over 295 times since 1966.]

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"Around 1962, soon after I started as an instructor at the University of Illinois, I became interested in collisional excitation of molecular vibrations. At that time, distorted wave theory was the method generally felt to be correct at low enough energy. It clearly failed at high energy giving transition probabilities greater than one. The question was, how low need one go before this approximation was correct? At this time, I was working on solving molecular structure problems on the computer, so it occurred to me that I could answer the question about the distorted wave problem by solving the scattering problem on a computer. I was surprised no one had tried it before. The only computer solutions were for special models, using methods which would only work on these models. Furthermore, the distorted wave approximation would not work for such models. I soon found out why no one had solved the problem before. The equations were terrifically unstable and could not be solved in a straightforward way.

"Bob Johnson joined my group as a graduate student in physics in about 1963. At that time, I was working on a general method to solve this problem and another student in my group was working on solving the problem for a special model for which the distorted wave approximation would work. I started Bob on another general approach which I had intended to try if the approach I was working on didn't work. He applied antenna theory to the problem, treating it as a radio wave scattering problem. When his work on scattering from discrete antennae appeared to be working, I dropped the approach I had been attempting and together we developed a technique which would work for any continuous potential. The first test of distorted waves that we tried after getting the method to work disagreed with distorted waves by a factor of more than 100 down to the excitation threshold. We were convinced this result could not be right. We eventually got a rather brute force approach to work which confirmed our surprising result. We studied the problem thoroughly and found systems for which the distorted wave approximation did work, and were able to give rules predicting the conditions under which the distorted wave approximation would work. After approximately four years of effort we finally had an approach which solved the general inelastic scattering problem.

"Immediately after publication of our paper we received a number of letters to the editor to referee implying that our results could not be correct. We prepared careful rebuttals to these letters, and in every case, when the authors of the letters read our rebuttals they withdrew their letters. Thus, none of this discussion ever appeared in the literature.

"There are two reasons why this paper is referred to so often. First, it presents exact results for a number of different situations. These quickly became a benchmark set of exact solutions against which new numerical methods or new approximations could be tested. Second, it demonstrated that scattering problems could be solved accurately numerically, and this paper may be considered the start of the field of computational scattering theory. An excellent and up-to-date book on this field is *Atom-Molecule Collision Theory.*"[1]

1. **Bernstein R B,** ed. *Atom-molecule collision theory: guide for the experimentalist.* New York: Plenum Press, 1979. 779 p.