This Week's Citation Classic

Centrifugal effects on a rotating molecule are represented by higher-degree terms in the rotational Hamiltonian function. This paper shows that the Hamiltonian can be transformed so that, for a completely unsymmetrical molecule, there are only (n+ 1) terms for each even degree n. [The *SCI®* indicates that this paper has been cited over 305 times since 1967.]

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"This must be one of the least intelligible papers to land in these columns. It is concerned with the rotational energy levels of a slightly elastic body in quantum mechanics. This is often a good model of a rotating molecule, and the energy levels can be determined from its spectrum. Given the energy levels, what can we say about the elastic constants?

"For a rigid body the energy is a quadratic function of the angular momentum, depending on the three principal moments of inertia. The centrifugal effects of non-rigidity are represented by adding terms of higher even degrees to the Hamiltonian energy function, since time-reversal symmetry forbids odd degrees. From a given Hamiltonian function it is fairly straightforward to compute its energy levels quantum mechanically and compare with the observed spectrum. The problem is to invert this procedure, and deduce from the spectrum the moments of inertia and centrifugal parameters of the molecule. For this inverse procedure, what is the correct number of independent terms of each degree? At the time, a classic paper of Kivelson and Wilson[1] gave six fourth-degree terms. The immediate stimulus to my work was a paper by Chung and Parker[2] which gave 105 sixth-degree terms. This was correct for their problem, but many of the terms made similar contributions to the energy levels. I set out to reduce the number as far as possible, little expecting to end up also reducing the Kivelson-Wilson number. In the first place, their type of considerations reduced the sixth-degree number from 105 to a more manageable ten. However the previous workers had overlooked a further point, namely that certain variations of the parameters produced the same changes in the Hamiltonian as unitary transformations, and so did not affect the energy levels. For a unique solution of the inversion problem, the number of independent terms had to be reduced. The final result was five fourth-degree terms, seven sixth-degree terms, and in general (n+1) terms of degree n.

"This may sound obscure, and it did to the referee. He had the impression that the paper 'loses much in intelligibility' by trying to be too general, and that 'this version will have to await exegesis.' The submitted version was actually my third writing, and the unintelligibility was probably increasing as I became more concerned with minutiae. Perhaps I should have returned an earlier version. Fortunately (?) a slightly amended version was accepted.

"Why has it become a *Citation Classic?* One possible answer is that the argument may have been abstruse but the conclusions were simple. But I think there was also a strong element of fortuitously good timing. The paper appeared just when computers were becoming fast enough to handle the computations conveniently and were becoming widely used by spectroscopists. Previously, microwave spectroscopists had tended to measure a few lines of low angular momentum to minimise centrifugal effects. Just when the problem of the excess parameters was becoming recognised,[3,4] the paper provided a solution."

1. **Kivelson D & Wilson E B, Jr.** Approximate treatment of the effect of centrifugal distortion on the rotational energy levels of asymmetric-rotor molecules. *J. Chem. Phys.* **20**:1575-9, 1952.
2. **Chung K T & Parker P M.** Higher-order centrifugal-distortion effects in asymmetric rotators. *J. Chem. Phys.* **43**:3865-8, 1965.
3. **Dreizler H & Dendl G**. Erfahrungen bei der Analyse der Zentrifugalaufweitung in Rotationsspektren. 1. Dimethylsulfoxyd. Z. *Naturforsch. A* **20**:30-7, 1965.
4. **Dreizler H & Rudolph H D.** Erfahrungen bei der Analyse der Zenirifugalaufweitung in Rotationsspektren.
2. Dimethylsulfid. Z. *Naturforsch. A* **20**:749-51, 1965.