This Week's Citation Classic® CC/NUMBER 13 MARCH 27, 1989

Hirschfelder J O, Byers Brown W & Epstein S T. Recent developments in perturbation theory. *Advan. Quantum Chem.* 1:255-374, 1964.
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This paper summarized what was known in 1964 about Rayleigh-Schrödinger type perturbation equations and their variational solutions. The topics considered include variational energy bounds, interchange theorems for double perturbations, fast converging iteration procedures, almost degenerate perturbations, techniques for deriving sum rules and evaluating sums, the Hartree-Fock approximation for atoms, and the existences and convergence of perturbative series. [The *SCI*® indicates that this paper has been cited in over 615 publications.]

Rayleigh-Schrödinger Perturbation Equations

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November 20, 1988

I still think this paper is useful. We had intended for it to be the basis for a book on perturbation theory. However, after Bill Byers-Brown left the University of Wisconsin to become professor of chemistry at the University of Manchester, we were never able to complete the book. Instead, I wrote a widely used series of papers with Phillip R. Certain on almost degenerate perturbations,[1-3] based on a technique that Bernie Kirtman developed (and a later short paper on the application of the technique[4]). I am sure that it can be improved to take advantage of the capabilities of present computers.

In 1972 Saul T. Epstein wrote a paper with Peter W. Langhoff and Martin Karplus[5] that showed how to eliminate the divergencies and secular terms that occur in time-dependent perturbation treatments. This should be a *Citation Classic*.

Two years later Saul published a book on *The Variation Method in Quantum Chemistry*.[6] (As Leibnitz said, "Since this is the best [or worst] of all possible worlds, the laws of physics can best be described by variational principles!") Saul does a good job of explaining the formal applications of variational techniques to a variety of problems. It is very useful, but it only devotes eight pages to time-dependent problems (which have become increasingly important) and it has very little discussion of almost degenerate perturbations.

I believe that the paper that Morton A. Eliason and I wrote[7] on the general collision theory treatment for bimolecular gas phase reactions should be a *Citation Classic* since Dick Bernstein and a few others have told me that it was helpful in developing the theory of molecular beam experimentation.

[Editor's note: Among the papers that have recently cited Hirschfelder's work are those by G. Bulk and R.J. Jelitto[8] and G. Chałasiński and M.M. Szczęśniak.[9]]

1. **Certain P R & Hirschfelder J O.** New partitioning perturbation theory. I. General formalism. *J. Chem. Phys.* 52:5977-87, 1970. (Cited 45 times.)
2. **Certain P R, Dion D R & Hirschfelder J O.** New partitioning perturbation theory. II. Example of almost degeneracy. *J. Chem. Phys.* 52:5987-92, 1970. (Cited 10 times.)
3. **Certain P R & Hirschfelder J O.** New partitioning perturbation theory. III. Applications to electron exchange. *J. Chem. Phys.* 52:5992-9, 1970. (Cited 35 times.)
4. **Hirschfelder J O.** Almost degenerate perturbation theory. *Chem. Phys. Lett.* 54:1-3, 1978. (Cited 10 times.)
5. **Langhoff P W, Epstein S T & Karplus M.** Aspects of time-dependent perturbation theory. *Rev. Mod. Phys.* 44:602-44, 1972. (Cited 175 times.)
6. **Epstein S T.** *The variation method in quantum chemistry*. New York: Academic Press, 1974. 276 p. (Cited 165 times.)
7. **Eliason M A & Hirschfelder J O.** General collision theory treatment for the rate of biomolecular, gas phase reactions. *J. Chem. Phys.* 30:1426-36, 1959. (Cited 240 times.)
8. **Bulk G & Jelitto R J.** A modified perturbation theory: iterative partitioning of the hamiltonian. *Phys. Lett. A* 133:231-8, 1988.
9. **Chałasiński G & Szczęśniak M M.** On the connection between the supermolecular Møller-Plesset treatment of the interaction energy and the perturbation theory of intermolecular forces. *Mol. Phys.* 63:205-24, 1988.

JA-14