

Manne R & Åberg T. Koopmans' theorem for inner-shell ionization.

*Chem. Phys. Lett.* 7:282-4, 1970.

[Department of Quantum Chemistry, University of Uppsala, Sweden]

Inner-shell ionization energies calculated from Koopmans' theorem are shown, by the sudden approximation, to relate to a weighted average energy for singly and multiply excited states in the photoelectron spectrum. This result is analogous to the Franck-Condon principle in molecular spectroscopy. [The *SCI*® indicates that this paper has been cited in over 250 publications.]

## A Theorem for Photoelectron Spectroscopists

Rolf Manne  
Department of Chemistry  
University of Bergen  
N-5007 Bergen  
Norway

Teijo Åberg  
Laboratory of Physics  
Helsinki University of Technology  
SF-02150 Espoo  
Finland

December 20, 1989

In the late 1960s, photoelectron spectroscopy made it possible to measure all those ionization energies that came out of quantum-mechanical calculations of atomic and molecular electronic structure. The leading experimental group working with ionization of tightly bound electrons was that of Professor Kai Siegbahn at the Institute of Physics, University of Uppsala. Siegbahn shared the Nobel Prize in chemistry in 1981 for his developments in this field.

As a graduate student at the neighbouring Department of Quantum Chemistry, Rolf Manne (RM) had done theoretical work on core-level chemical shifts, partly together with the Siegbahn group.<sup>1</sup> Teijo Åberg (TÅ) joined the Uppsala quantum chemists as a Nordita fellow after his thesis work on applications of the sudden approximation (SA) to core-electron emission processes. In this way he approximated the

response of the outer electrons to the removal of a core electron as being the consequence of the sudden change between two time-independent Hamiltonians. Previously, he had used SA for an interpretation of the origin of X-ray satellites.<sup>2</sup> One should add that we, as doctoral candidates, were essentially unsupervised.

In the late 1960s, several unclear ideas of "electron relaxation" were being debated. Our paper resolved that debate by giving a description using basic quantum-mechanical principles.

The main result of the paper, that a core orbital energy calculated for the neutral group state should not be interpreted as a single ionization energy (Koopmans's theorem) but as a weighted average of such energies, is a simple consequence of SA. After discussions with TÅ in the summer of 1968, RM got his first insight of this in the spring of 1969.

We wrote the paper together in 1970 while TÅ had his fellowship in Uppsala and where RM was finishing up his doctoral thesis. We modelled our work upon the original *Physical Review* paper by E.U. Condon on the simultaneous electronic and vibrational excitation of diatomic molecules.<sup>3</sup> In fact, RM kept that volume of *Physical Review* open on his cluttered desk while the paper was being written.

Independently, B.I. Lundqvist<sup>4</sup> and D.C. Langreth<sup>5</sup> proved that the creation of a core hole in metals gives rise to a photoemission spectrum with an average energy equal to the orbital energy. They obtained their results using a model Hamiltonian that includes coupling between the core hole and the plasmons. Although we knew Lundqvist in Gothenburg, neither he nor we realized that we had come to the same conclusion regarding electron relaxation until much later. Still earlier, P. Nozières had found a similar relationship<sup>6</sup> but did not explore it.

Our paper has been cited both for the result referred to in the title and as a standard reference to the SA in photoelectron spectroscopy. We believe that our paper caught on because we considered a better-known experimental situation and because our theoretical apparatus could more easily be understood by experimentalists.

In 1970 the number of reprint requests could still be used to measure scientific impact. RM, who had earlier got large numbers of requests for less exciting work on molecular orbital theory, wagered a bottle of German Steinwein with TÅ that we would get 100 requests during the first year. We never got more than 60 or 70. Was this due to the small number of people in electron spectroscopy at that time, or were more people finding photocopying easier?

1. Siegbahn K, Nordling C, Johansson G, Hedman J, Hedén P F, Hamrin K, Gelius U, Bergmark T, Werme L O, Manne R & Baer Y. *ESCA applied to free molecules*. Amsterdam, The Netherlands: North-Holland, 1969. 200 p. (Cited 1,480 times.)
2. Åberg T. Theory of X-ray satellites. *Phys. Rev.* 156:35-41, 1967. (Cited 210 times.)
3. Condon E U. Nuclear motion associated with electronic transitions in diatomic molecules. *Phys. Rev.* 32:858-72, 1928. (Cited 225 times since 1945.)
4. Lundqvist B I. Characteristic structure in core electron spectra of metals due to the electron-plasmon coupling. *Phys. Kondens. Mater.* 9:236-48, 1969. (Cited 105 times.)
5. Langreth D C. Singularities in the X-ray spectra of metals. *Phys. Rev. B—Condensed Matter* 1:471-7, 1970. (Cited 160 times.)
6. Nozières P. *Theory of interacting Fermi systems*. New York: Benjamin, 1964. p. 350. (Cited 445 times.)