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This Week's Citation Classic

Grimley T B. Electronic structure of adsorbed atoms and molecules. *J. Vac. Sci. Technol.* **8**:31-8, 1971. [Donnan Labs., Univ. Liverpool, Liverpool, England]

Through chemisorption, originally discrete energy levels of the adsorbate are changed into resonances. The calculation of these resonances is described, and the conditions under which the concept of a 'surface molecule' becomes valid are examined. [The *SCI*® indicates that this paper has been cited over 75 times since 1971.]

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"This was an invited paper presented at the National Symposium of the American Vacuum Society held in Washington, DC in October 1970. It was based on my research carried out at Liverpool University during 1966-70. W.E. Garner (Bristol University) had aroused my interest in chemisorption theory some ten years earlier. But I think that the stimulus to begin serious work using second quantization and Green functions was an invitation to participate in the 'study week' of the Pontifical Academy of Sciences on the subject 'Molecular Forces,' which was held in April 1966. There I compared the interaction between adatoms with the retarded van der Waals interaction in the gas phase.

"The central requirement of a theory of chemisorption was to show how a localized bond could be formed between an atom and a metal substrate. It was accepted that the metal substrate was to be described by an itinerant electron model, yet much of the experimental data from chemisorption and catalysis could be interpreted most easily in terms of the existence of surface complexes with bonds similar to gas-phase counterparts. The suggestion that only surface, i.e., localized, states of the substrate were used in chemisorption was not convincing because such states were not thought to be sufficiently common. Also, the more general observation that the disturbance of the metal electrons would be localized by the very efficient screening, seemed to make the localization of electrons in the chemisorption bond depend on electron-electron interaction phenomena familiar in the theory of metals but not in that of small molecules. In fact, I[1] and J. Koutecky'[2] had shown many years before that even the simplest LCAO-MO schemes allow for the formation of a localized bond between an atom and a metal surface. The trouble was that the mathematical formalism needed to handle the quasi-continuum of substrate levels (Green functions or resolvent operators) was not as familiar then as it is now. What was needed was a discussion of some simple chemisorption systems which showed how quantum chemistry and the theory of electrons in metals were merged in chemisorption theory. This is what I did, and I used a theoretical model which contained the essential features of bond formation between a metal with itinerant electron states, and an atom with localized ones, in the simplest possible way. I also showed how, for one system, the notion of a surface complex can be theoretically justified, and how for another, it cannot.

"One reason why this paper has been cited so often is that it appeared at a time when surface physics, and modern surface chemistry, were expanding rapidly. On the other hand I did try to make a difficult subject intelligible. Perhaps I succeeded."

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1. **Grimley T B.** The molecular orbital theory of the interaction between an atom and a crystal surface. *Proc. Phys. Soc. London* **72**: 103-15, 1958.
2. **Koutecký J.** Ergebnisse einer studie über chemisorption mit hilfe der methode der moleküleigenfunktionen. Z. *Elektrochem.* **60**:835-8, 1956.