

This results, to a very good approximation, in a small Schrödinger kitten state of the remaining light pulse. Finally, they used a high-quality homodyne detector to measure the state of the pulse (more precisely, its Wigner function, which is a special kind of probability distribution in phase space). The mean photon number in the pulse is slightly less than one. This seems disappointingly small. However, the light pulse is in a coherent state (more precisely, in a superposition of two coherent states), and coherent states are

themselves superpositions of states with arbitrarily high photon numbers. In order to compare their results with simulations, the authors had to expand the coherent states up to photon-number states with five photons.

Five photons may still seem like a very dim pulse, but it is actually bright enough to be seen with the naked eye (when at the optimal wavelength). Furthermore, the theorists know how to breed Schrödinger cats from kittens using linear optics. Hence, in principle, the race toward larger and larger Schrödinger cat

states is on, although the technical path is full of pitfalls. The question of whether there is a fundamental size limit to Schrödinger cat states remains open.

References

1. A. Auffeves *et al.*, *Phys. Rev. Lett.* **91**, 230405 (2003).
2. A. Ourjoumteev, R. Tualle-Brouri, J. Laurat, P. Grangier, *Science* **312**, 83 (2006); published online 9 March 2006 (10.1126/science.1122858).
3. D. Bouwmeester, A. K. Ekert, A. Zeilinger, Eds., *The Physics of Quantum Information* (Springer-Verlag, Berlin, 2000).

10.1126/science.1125584

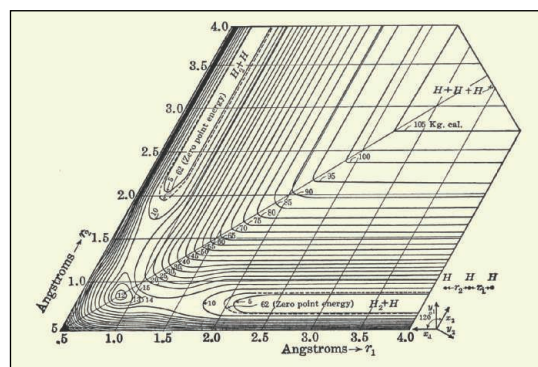
CHEMISTRY

Chemistry in a Computer: Advancing the *in Silico* Dream

Alec M. Wodtke

Imagine that laboratory chemists might one day sit down at a computer, punch in data characterizing a new reaction of potential industrial importance, and receive computer output describing the likely reaction rates, temperature and pressure conditions required, and possible catalysts that would speed up the reaction rate to useful speeds. Although still only a dream, such a tool is beginning to take shape, at least in a rudimentary form. Indeed, as Nieto *et al.* report on page 86 of this issue (1), we are slowly but surely reaching the long-sought goal of using first-principles theory, based firmly in quantum mechanics, to predict the properties of chemical reactions at metal surfaces. Such reactions underlie all of heterogeneous catalysis.

The so-called standard model of chemical reactivity was first described by Michael Polanyi and Henry Eyring in 1935, when they realized that the Born-Oppenheimer approximation could be used to dramatically simplify the solution to the many-body Schrödinger equation, the most fundamental law of quantum mechanics for chemical reactions (2). This brilliant insight, overlooked by the Nobel committee in perhaps the greatest oversight in the history of the chemistry prize, led Eyring and Polanyi to the computational machinery that allows construction of a potential energy surface describing all of the forces between the atoms taking place in any chemical reaction

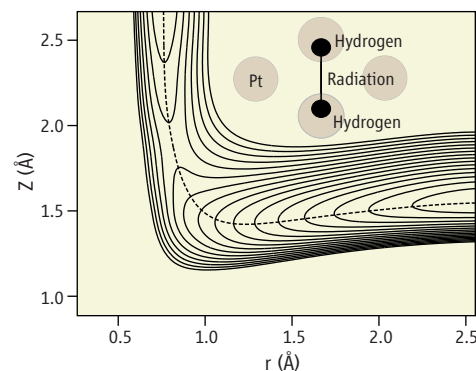


Reaction models. (Left) The first potential energy surface for a chemical reaction was devised in 1935 to explain the simplest $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ reaction. (Right) Today, theoretical chemists are able to accurately explain reactions occurring at the surface of a bulk metal, providing a quantitatively accurate look at the inner workings of reactions important to heterogeneous catalysis.

(see the figure). Knowledge of the interatomic forces allows accurate computer simulations of chemical reactions, in principle providing every knowable characteristic of that reaction under any conceivable set of reaction conditions. Since that time, our methods for solving Schrödinger equations—especially the advent of density functional theory (3)—have advanced by leaps and bounds. Development of ever more powerful computers has accelerated the rise in importance of theoretical chemistry. Some remarkable successes include the quantitative agreement between experiment and theory for the prototypical $\text{H} + \text{HD} \rightarrow \text{H}_2 + \text{D}$ reaction (4) and the advent of the successful use of theoretical advice for new industrial heterogeneous catalyst development (5).

Understanding reactivity at solid surfaces, especially surfaces that are models for heterogeneous catalysis, is an extremely exciting forefront area of modern research. As heterogeneous catalysis is involved in about one-

Theoretical studies of chemical reactions often make the simplifying assumption that the motion of atoms is not coupled to the motion of their electrons. While this assumption is questioned for reactions on metal surfaces, it is useful for describing hydrogen reactions on platinum.



The author is in the Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106, USA. E-mail: wodtke@chem.ucsb.edu

angstroms in size ensures that they move much more rapidly than the atomic nuclei. For metallic (conduction) electrons in solids that are delocalized over large distances, electron translational energies can be much smaller and the separation of time scales need not necessarily hold.

In recent years there has been a flurry of new work casting doubt on the validity of the Born-Oppenheimer approximation for reactions at metals. These include the failure of the standard model to accurately account for the experimentally observed N_2 vibrational excitation in the recombination of N atoms desorbing from ruthenium (6) and in another case the incidence energy dependence of O_2 dissociative adsorption on aluminum (7, 8). In our laboratory, we performed experiments showing that hundreds of kilojoules of vibrational energy per mole can be transferred from a “hot molecule” to electrons of a metal; this work culminated in the observation of vibrational promotion of electron emission from a metal with a low work function (9, 10). This result showed explicitly, by direct detection of the hot electron essentially blown off the surface by the force of the molecular vibration, that the Born-Oppenheimer approximation broke down. The topic of Born-Oppenheimer breakdown has become an active forefront area of research in surface chemistry.

Nieto *et al.* show that despite these clear indications of the importance of Born-Oppenheimer breakdown, one is not precluded from using the standard model of reactivity in all cases. In other words, there certainly are some reactions at metal surfaces (perhaps most; time will tell) that are well described by the standard model of reactivity. In this work, comparisons are made between experiment and theory in one of the simplest and best characterized surface chemical reactions, H_2 interacting with a platinum surface. It is noteworthy that Nieto *et al.* are able to use a highly sophisticated version of the standard model, where six degrees of freedom are treated quantum mechanically—a technical tour de force. The 6D quantum approach is essential because H_2 and H exhibit quantum interference (wave behavior) effects as a result of their low masses. When H_2 collides with platinum, it may bounce off and diffract quantum mechanically or dissociate, forming adsorbed H atoms on the surface. The first-principles simulation of H_2 on platinum reported by Nieto *et al.* captures in a nearly quantitative fashion both of these very different kinds of collisional processes. This is a remarkable success for the standard model of reactivity and provides new motivation to seek the limits of this approach, which have not yet been identified clearly.

Future work will certainly focus on helping to better define under what conditions the standard model of reactivity can be applied to catalytically important reactions at metal surfaces. In addition, theorists are actively striving to develop the next generation of chemical simulation packages that can take into account the role of excited electronic states in surface chemistry, going beyond the Born-Oppenheimer approximation. Such developments will make important contributions to our understanding of all kinds of chemistry involving excited electrons in solids. For example, our ability to learn how to power catalytic processes with light (photocatalysis) as opposed to heat (conventional thermal catalysis) will rely on new understanding of excited states in solids, an area of future technology that is essential to a world with diminishing cheap oil reserves.

References

1. P. Nieto *et al.*, *Science* **312**, 86 (2006); published online 9 February 2006 (10.1126/science.1123057).
2. H. Eyring, M. Polanyi, *Z. Phys. Chem. B* **12**, 4 (1935).
3. See, for example, the review by W. Kohn, A. D. Becke, R. G. Parr, *J. Phys. Chem.* **100**, 12974 (1996).
4. S. D. Chao *et al.*, *J. Chem. Phys.* **117**, 8341 (2002).
5. C. J. H. Jacobsen *et al.*, *J. Catal.* **205**, 382 (2002).
6. L. Diekhoner *et al.*, *J. Chem. Phys.* **117**, 5018 (2002).
7. J. Behler *et al.*, *Phys. Rev. Lett.* **94**, 036104 (2005).
8. A. Hellman *et al.*, *Surf. Sci.* **532**, 126 (2003).
9. Y. H. Huang, C. T. Rettner, D. J. Auerbach, A. M. Wodtke, *Science* **290**, 111 (2000).
10. J. D. White *et al.*, *Nature* **433**, 503 (2005).

10.1126/science.1124924

DEVELOPMENTAL BIOLOGY

Mixed Messages in Early Development

Stephen M. Cohen and Julius Brennecke

During oogenesis, the egg is loaded with nutrients, proteins, and messenger RNAs (mRNAs) produced in the ovary by the mother. Many of these “maternal mRNAs” encode proteins that are needed for early development of the embryo, before the onset of new mRNA synthesis that is directed by the embryo’s own genome. Soon after fertilization of the egg, a transition occurs from use of maternal mRNAs to expression of the zygotic genome (see the figure). On page 75 of this issue, Giraldez and co-workers report that the zebrafish microRNA-430 (miR-430) family contributes to this transition by promoting turnover of maternal mRNAs (1).

MicroRNAs (miRNAs) are small noncoding RNAs that serve as posttranscriptional regula-

tors of gene expression (2, 3). They provide sequence information needed to guide ribonucleoprotein complexes (miRNPs) to target mRNAs, leading to repression of their translation and enhanced turnover. The 5' end of a miRNA, called the seed region, confers much of the target recognition specificity. Computational and experimental studies have shown that miRNAs typically have hundreds of target sites in a given transcriptome, most often located in the 3' untranslated region (3' UTR) of a target mRNA (4–7). Recent studies based on miRNA target prediction and on comparison of miRNA and target mRNA expression suggest that miRNAs may help to reduce expression of mRNAs to inconsequential levels in cells where they are no longer needed or where their expression might be detrimental (8, 9).

The new findings by Giraldez *et al.* provide an elegant example of this principle in action.

MicroRNAs, molecules that repress gene expression, fine-tune early embryogenesis. Rather than expressing genetic information supplied in the egg from the mother, microRNAs direct the developing embryo to express its own genome instead.

In previous work (10), they identified miR-430 as an abundant early expressed miRNA in the developing zebrafish embryo. Subsequent cloning efforts showed that miR-430 is the only abundant miRNA in the first 4 to 8 hours of development (11). miR-430 is encoded by a large gene family (more than 90 members) that produces several, slightly different, forms of the mature miRNA. Because these miRNAs are expressed at the same time and place and share the same seed sequence, they are expected to have largely overlapping sets of targets. Expression of miR-430 begins at the moment of transition from maternal to zygotic gene expression, and mature miR-430 rapidly accumulates to high levels.

In view of the complexity of the miR-430 gene family, generating mutant zebrafish that lack it would be a daunting task. However, because this miRNA is the only one expressed

The authors are at the European Molecular Biology Laboratory, Heidelberg, Germany. E-mail: cohen@embl.de