A solid-state failure of the Born–Oppenheimer approximation

According to a keystone principle of molecular physics, atoms striking semiconductor surfaces shouldn't excite surface electrons. But they do.

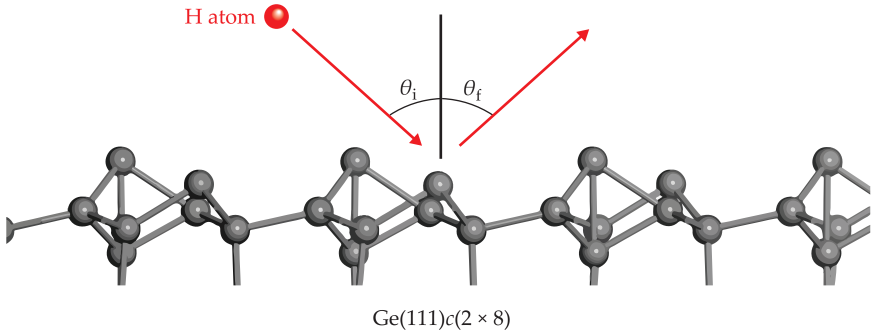

FIGURE 1. TO TEST THEORY against experiment in surface chemistry, researchers study a simple atom–surface interaction: bouncing hydrogen atoms against a solid surface at a specified speed and incidence angle θ_i, and measuring the speed and angle θ_f of the scattered atoms. The surface shown here is the (111) crystal surface of germanium in the reconstruction denoted by $c(2 \times 8)$. (Courtesy of Kerstin Krüger.)

Electrons are light and quick; atomic nuclei, comparatively, are heavy and slow. The gap in mass and time scales means that electronic and nuclear dynamics can usually be considered separately, as Max Born and J. Robert Oppenheimer pointed out in a 1927 paper[1] that has heavily influenced how chemical physicists think about atoms and molecules to this day: Electrons gracefully flit around ponderous nuclei and instantaneously follow them wherever they go.

The intuitive Born–Oppenheimer picture doesn't always hold, but it generally does a pretty good job. And in situations where it does break down, it's usually clear what's going on. In some chemical reactions, for example, the nuclei are known to rearrange too rapidly for the electrons to keep up (see PHYSICS TODAY, August 2021, page 14).

Now, however, Kerstin Krüger of Georg-August University in Göttingen, Germany; her PhD advisers, Oliver Bünermann and Alec Wodtke; and their colleagues have found that in at least some interactions between atoms and solid surfaces, the Born–Oppenheimer approximation isn't just a little bit off—it fails dramatically. And they're not quite sure why.

The researchers fired hydrogen atoms at the surface of germanium, a semiconductor, and found that a large fraction of the atoms were losing a significant portion of their energy.[2] A close look at the data suggested that the atoms were whacking Ge surface electrons hard enough to excite them from the valence band into the conduction band. Under the Born–Oppenheimer approximation, that's not supposed to happen. The electrons are supposed to be nimble enough to get out of the way.

Testing theory

If not for the Born–Oppenheimer approximation, computational chemistry might never have gotten off the ground. To simulate the dynamics of a molecule, researchers would need to solve the multiparticle time-dependent Schrödinger equation to compute the dynamics of all of the nuclei and electrons simultaneously.

Thankfully, they don't have to do that. Instead, they can consider the nuclei to be moving around in a potential-energy landscape created by the electrons. The means of estimating that potential have grown over the years in sophistication and accuracy (see PHYSICS TODAY, December 2013, page 13), from empirical interatomic potential-energy functions to fully quantum calculations of the electrons' actual energy. What they have in common, though, is the assumption that the electrons can keep up with the nuclei: The potential energy is a function of where the nuclei are, not where they've been or where they're going.

Molecular-dynamics simulations have yielded many valuable insights into microscopic molecular motions on a level that's not accessible to experimental methods. But it's important to keep testing their results against experiments in order to make sure they're giving the right answers and that their assumptions are warranted.

Several years ago, Bünermann and colleagues observed that there was a gap in researchers' understanding of how well molecular dynamics simulations apply to chemical reactions at solid surfaces. Surface reactions are widely used in industrial chemistry, to profound effect on humanity (see PHYSICS TODAY, September 2018, page 17). But they're famously messy, and the challenge in testing experiments against theory is to find surface processes that are both experimentally feasible and theoretically tractable.

Most surface reactions involve polyatomic molecules, whose many degrees of freedom make them complicated to model. On the other hand, single reactive atoms (that is, not noble gas atoms) can be experimentally challenging: They can't just be pulled out of a bottle, so researchers need to make them on the fly by breaking apart molecules.

The experimental apparatus for dissecting the simple atom–surface interaction shown in figure 1—shooting H atoms at a surface with a specified speed and direction and measuring the speed and direction at which they bounce back—required a specialized combination of components, and it had never been built before. So Bünermann and colleagues built it.[3] And they've been using it to study H-atom scattering off all sorts of surfaces.

Mysterious excitations

The apparatus was designed to hunt for violations of the Born–Oppenheimer approximation. "The approximation has always been on our mind," says Bünermann, "because H atoms sometimes stick to surfaces. So there must be a violation somewhere, because otherwise all the atoms would just bounce back."

When the researchers fired H atoms at a metal surface, for example, they observed a minor deviation from the Born–Oppenheimer approximation that they could account for with a perturbative correction: Electrons at the surface be-

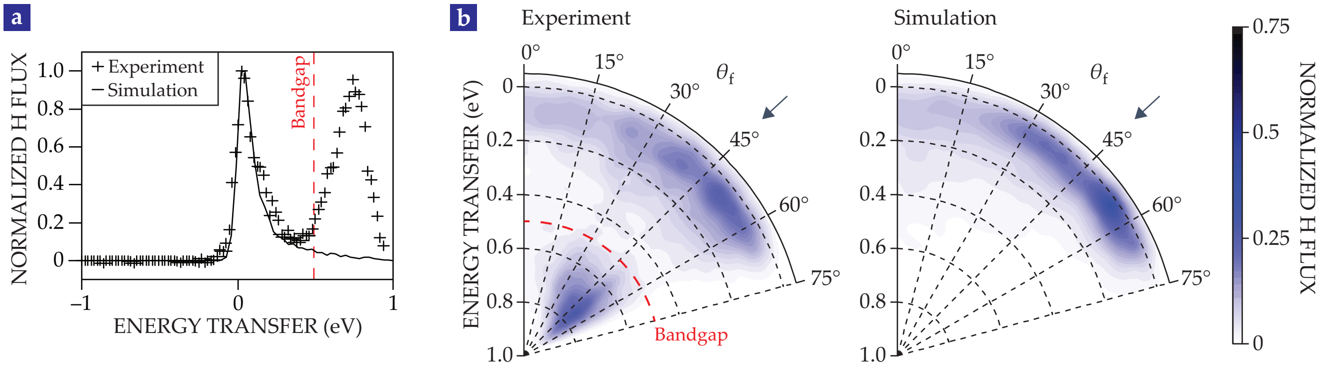

FIGURE 2. THE ENERGY DISTRIBUTIONS of hydrogen atoms scattering off a germanium surface reveal an unexpected peak. **(a)** Atoms with an initial energy of 0.99 eV and an initial angle of 45° emerge in a bimodal distribution of energies: Some atoms lose just a little energy to the surface, while others lose a lot. The first peak is quantitatively accounted for in molecular-dynamics simulations, but the second peak is completely absent. **(b)** Data for the same experiment and simulation are resolved according to the scattering angle θ_f. The dashed red line is the Ge surface bandgap. (Adapted from ref. 2.)

haved like a viscous fluid that exerted a drag force on the intruding H atoms.[4] As a result, atoms bouncing off the surface emerged with less energy than they otherwise would have. Some of them lost all their energy, and they remained on the surface.

In the new experiments on semiconductor surfaces, however, the electron-drag theory doesn't apply: Electrons can't act like a viscous fluid when they're locked into a regimented set of valence-band quantum states. So Bünermann and colleagues expected the Born–Oppenheimer approximation to hold—but that's not what they observed. As shown in figure 2a, the scattered atoms have a bimodal energy distribution. Some atoms lose just a little of their energy when they bounce off the surface. Others lose a lot.

The first of those peaks is quantitatively reproduced by the molecular-dynamics simulations performed by Bünermann's collaborators Yingqi Wang and her adviser, Hua Guo, at the University of New Mexico, and it's fully consistent with the Born–Oppenheimer approximation. But the simulations don't reproduce the second peak at all.

One way that atoms could lose so much energy is if they stick to the surface, thermalize, and desorb. But from a look at the atoms' angular distributions, Bünermann and colleagues are pretty sure that that's not what's happening. As shown in figure 2b, atoms in both channels scatter at angles θ_f close to the incidence angle $\theta_i = 45°$. If the atoms were thermalizing and desorbing, one would expect a much broader angular distribution independent of θ_i.

The researchers have two reasons for concluding that the mysterious peak is due to H atoms exciting Ge electrons from the valence band into the conduction band. First, in all their experiments, the peak sets in just above Ge's surface bandgap of 0.49 eV. Second, when they increase the H atoms' initial energy, the peak gets bigger. In the experiments shown in figure 2, about half of the atoms with an initial energy of 0.99 eV emerge in the unexplained high-energy-transfer channel. But for an initial energy of 6.17 eV, that portion jumps to more than 90%. If the atoms excite electrons because they're moving too fast for the electrons to get out of the way, it stands to reason that speeding up the atoms would increase the magnitude of the effect—just what the researchers see.

Beneath the surface

Bünermann and colleagues' published experiments focus on the Ge(111) surface, because it's the easiest semiconductor surface for Wang and Guo to tackle in their simulations. Crystal surfaces tend to undergo reconstruction—that is, their atoms rearrange into structures that differ from the bulk—and the Ge(111) reconstruction, denoted by "$c(2 \times 8)$," is well understood. But they've also performed experiments on several other semiconductor surfaces, including Ge(100) and the (111) and (100) surfaces of silicon. And they see essentially the same effect each time.

Although they don't yet have a theory that can quantitatively explain their observations, they're starting to understand why the atoms separate into two peaks. Because of the reconstruction, the Ge atoms at the surface aren't all chemically equivalent. "We're pretty sure that the branching is connected to which one of the different germanium environments the atom hits," says Bünermann.

The researchers are focused on the basic-research task of understanding the fundamental role of the Born–Oppenheimer approximation in surface chemistry. But they also have some ideas for how the phenomenon they've discovered might be applied. Because atom–semiconductor collisions promote electrons into the conduction band with surprising efficiency, the excited electrons might be detected electrically, which could be the basis for a new type of sensor.

The scattering experiment might also be adapted into a new technique for studying the electronic structure of surfaces. Plenty of techniques for looking at surfaces are already available, such as photoelectron spectroscopy and electron energy-loss spectroscopy, but their signals are sometimes influenced by bulk electrons too. "Here, we're sure that we're seeing only surface states," says Bünermann, "and those are normally not so easy to access."

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References

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