

A recent flurry of activity in hot-electron research demonstrates that these particles with high, far-from-equilibrium energies can be used in an increasingly large variety of applications. These include solar-energy harvesting¹⁰, sensing¹¹, catalysis, driving new types of chemical reaction^{12,13}, and the fabrication of new types of nanoscale electron source¹⁴. Moskovits and colleagues add to this set of applications by showing an intriguing and quite efficient photosynthetic device for which the oxidation and reduction reactions rely on hot-electron generation through the excitation of surface plasmons in Au nanowires. By coating the Au nanowires — in different sections —

with a Pt-decorated TiO₂ layer and a Co-based oxygen evolution catalyst, it is possible to run both the reduction and oxidation reactions, respectively, from the same nanostructure, thus producing a photosynthetic unit that does not require external wiring. The system shows long-term operational stability and could lead to new types of clean solar-energy harvesting device, fully exploiting the benefits of nanostructured electrodes. □

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MOLECULAR ELECTRONICS

Reflections on charge transport

By varying the distance between two electrodes bridged by a single molecule, the interaction between charges passing through the molecular junction and their mirror images in the metal contacts can be observed.

Georg Heimel and Jean-Luc Brédas

In the push towards the ultimate limit of miniaturization in technology, researchers are at present directing considerable efforts in trying to concentrate the functionality of an electronic, optoelectronic or mechanical device into a single molecule. Once suitable compounds have been designed and synthesized, they need to be ‘wired up’ to make a working device. Unfortunately, atomic-level variations in the geometry of the electrode–molecule contacts, which are notoriously hard to control, strongly affect the alignment of the molecular energy levels relative to the Fermi energy (E_F) of the metallic leads. And because the molecular states closest to E_F constitute the transport channels used by electrons to pass from one electrode to the other, the current flowing through the junction at a given bias voltage — which is the most basic parameter characterizing any electronic device — varies from sample to sample. Consequently, experimental determination of transport-level energies through electrical measurements often has to rely on statistical averaging^{1,2}, a method that can mask other contributions. Writing in *Nature Nanotechnology*³, Herre van der Zant and colleagues from the Delft University of Technology

and the University of Leiden in the Netherlands have now shown that, by combining mechanical^{4,5} and electrostatic gate control^{6,7} in individual molecular junctions, one of these previously hidden phenomena can be disentangled and reproducibly quantified: the image-charge effect.

When a point charge is placed at a distance z from a metal surface, it induces a polarization cloud of surface charges (Fig. 1a). From a simple electrostatic standpoint, the net electric field outside the metal can be described as that being due to the actual charge plus that due to its mirror image, that is, a point charge of opposite sign at a position $-z$ inside the metal (Fig. 1b). Because of the mutual attraction between the two, bringing a point charge closer to a metal surface lowers the energy of the system. Likewise, an extra charge injected into a neutral molecule that resides on a metal surface is energetically stabilized. In the case of adding an electron, the lowest unoccupied molecular orbital (LUMO) thus moves down in energy towards E_F with decreasing distance between molecule and surface (Fig. 1c). Conversely, when removing an electron (and thereby leaving a positive charge behind), the highest occupied molecular

orbital (HOMO) moves up in energy, that is, towards E_F as well.

When van der Zant and co-workers varied the spacing between two metal electrodes^{4,5} bridged by a phthalocyanine derivative, they observed that the energy of a single distinct transport level shifted significantly and reversibly over many open–close cycles. The shift was towards E_F on decreasing the electrode spacing and away from E_F on increasing it³ (Fig. 1d). However, to unambiguously attribute their observations to the image-charge effect, they also needed to demonstrate that these energy shifts pertained to both occupied and unoccupied transport levels. If they had exclusively monitored either one or the other across all their samples, they would not have been able to discriminate between the image-charge effect and different interfacial phenomena that shift all energy levels up or down rigidly with respect to E_F .

Adding electrostatic gate control^{6,7} to their set-up (Fig. 1d) provided the final piece in the jigsaw. As a consequence of variations in the atomic-level geometry of the metal–molecule contact, and therefore, in the transport-channel energies from junction to junction, the current indeed passed through HOMO-like states in some

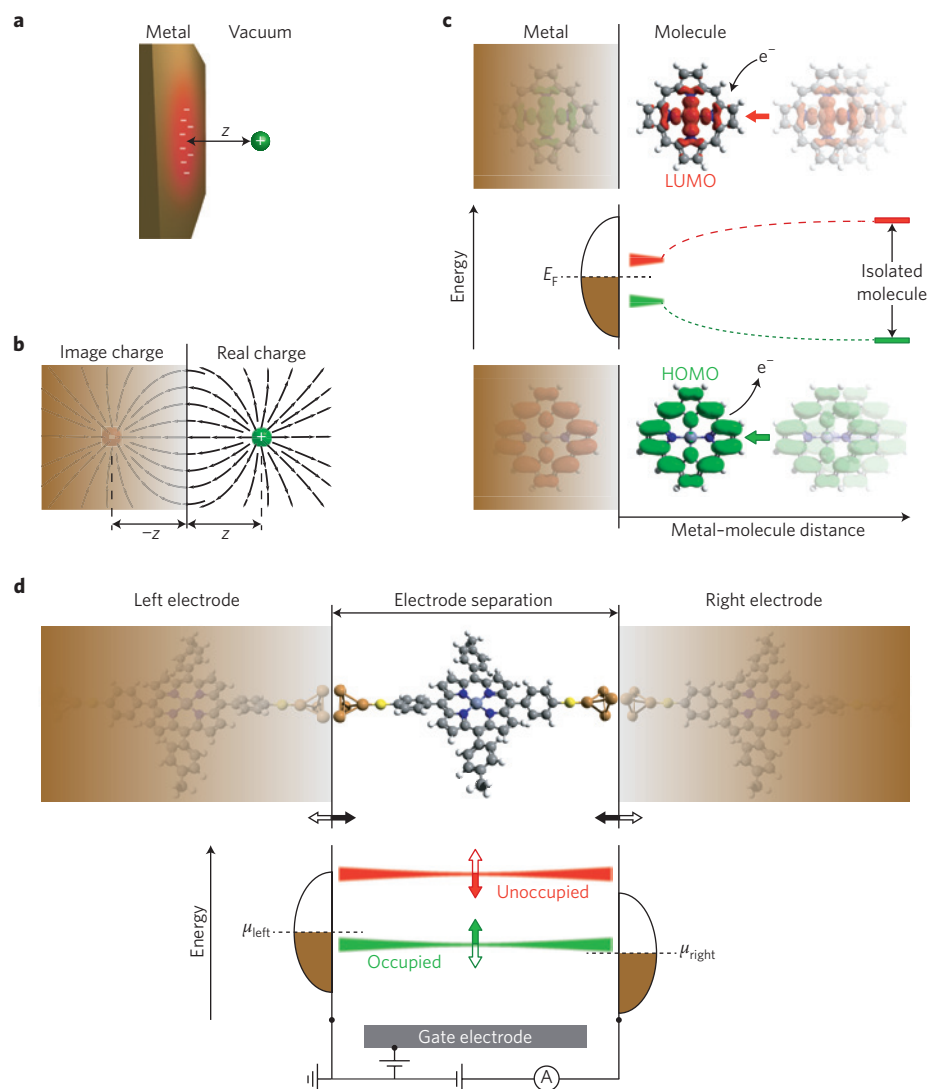


Figure 1 | Schematic of the image-charge effect. **a**, A positive charge (green) at a distance z from a metal surface induces negative (red) surface charges there. **b**, Electric field outside the metal (field lines indicated by arrows). **c**, The energy gained by putting an electron (e^-) onto a molecule increases as it approaches a metal surface. The LUMO thus shifts towards the metal E_F . Conversely, the energy cost for removing an electron from a molecule decreases. The HOMO thus shifts towards E_F as well. **d**, Electrons passing through a molecular junction feel their own image charges and the mirror images of the charge distribution in the neutral molecule. Reducing the electrode separation thus brings both the LUMO and the HOMO levels closer to E_F (filled arrows) whereas increasing it pushes them away from E_F (empty arrows). In contrast, applying a gate voltage shifts all states in the same direction, thus providing a means for determining whether current flows through occupied or unoccupied levels at a certain bias voltage (defined by the electron chemical potentials μ_{left} and μ_{right} in the respective electrodes).

samples and through LUMO-like states in others, in both cases responding to changes in electrode separation as only the image-charge effect can explain.

Furthermore, density functional theory (DFT) calculations showed that the conduction pathways in the present experiments did not correspond to the actual free-molecule HOMO or LUMO but, rather to hybrid states extending

from the electrodes onto the molecule³. In this context, it is important to note that common flavours of DFT cannot, as a matter of principle, capture the image-charge effect. In spite of its apparent simplicity in electrostatic terms, the effect is the consequence of non-local electron correlation. Incorporating such phenomena into atomistic first-principles simulations is computationally demanding,

and that this is feasible at all could be demonstrated only recently⁸, and only for molecules much smaller than that investigated by the Dutch group. Their results thus provide a benchmark for future theoretical efforts and underline that semiclassical models of the image-charge effect^{9,10} can go a long way, if based on the spatial distribution of a charge added to the entire molecular junction (which DFT is well suited to deliver).

Although being able to contact a single molecule and measure its charge-transport properties are significant achievements of nanotechnology, there is still much to learn regarding the interpretation of the data and their correlation to the molecular structure — information that then could be used to guide chemical synthesis of new molecules. As the work by van der Zant and colleagues demonstrates, simultaneous control of several experimental parameters, such as electrode separation and gate voltage, is a powerful strategy for extracting physically insightful information. A promising future direction would be to try to shift the electronic states responsible for charge transport from the metal–molecule contact onto the molecule itself, and then tune the localization of the molecular orbitals and their distance from the electrodes by chemical means. This strategy is likely to yield deeper insights yet, eventually allowing researchers to go from molecular design to targeted molecular-orbital design. □

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