IMAGING TECHNIQUES

Light scatters electrons to make holograms

The quantum interference of electrons that have been scattered by light has been used to produce holograms of the underlying electromagnetic fields — and might open up methods for studying materials at high temporal and spatial resolution.

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If you ask people what a hologram is, they'll probably describe the 3D light projections of science-fiction films — such as the vision of Princess Leia floating in free space in the 1977 film *Star Wars*. Such projections are becoming a reality[1], but the original goal of holography in science is arguably more mundane: to record a property of wave fields known as the phase, which defines the pattern of peaks and troughs of a travelling wave at a given moment in time. For many physicists, this concept is just as exciting as a sci-fi hologram. Writing in *Science Advances*, Madan *et al.*[2] report new types of hologram produced by the scattering of electrons by light fields. Not only do these findings broaden the scope of electron holography, but they also allow both the amplitude and the phase of electromagnetic (light) waves to be determined.

Holography is a widely used measurement technique in electron microscopy that makes use of the wave character of electrons[3]. In this technique, two parts of an electron beam are overlapped to create a stripy interference pattern (the hologram). The difference in the phases of the two beams can be extracted from this pattern. Because electrical and magnetic fields can affect the phases of electron beams that pass through them, holography in electron microscopy can be used to quantitatively map such fields with extremely high spatial resolution, down to the nanometre scale.

However, Madan *et al.* wanted to measure the phase of oscillating light waves. To this end, they developed a holographic method that depends on a different principle from that used in conventional electron microscopy: the modulation of quantum interference between electrons by oscillating light fields. Let's consider the physical mechanism by which electrons interact with light in the authors' experiments.

If a stream of fast electrons traverses an oscillating electromagnetic field, some electrons accelerate whereas others decelerate, depending on when they enter and exit the field. Measurements of the velocity distribution of electrons that have passed through such a field have revealed that electrons pick up or lose energy in quantized amounts — specifically, in multiples of the energy of the photons in the light field[4,5]. The size of the effect increases with the light intensity, a relationship that is used as the basis of a technique called photon-induced near-field electron microscopy (PINEM) to map light intensities around nanoparticles and other small structures[6].

To measure the phase of light waves in PINEM experiments, some form of interference must be produced. Madan *et al.* created such interference by conducting PINEM experiments on samples that had different geometries, and in which the electrons interacted with more than one light wave. Some of these implementations involved electrons sequentially flying through two spatially separated light fields. As has been shown previously[7], the relative phase of these two fields determines the strength of the combined electron–light interactions: in-phase fields can enhance the interaction in a kind of constructive interference, whereas the two fields can cancel each other out if they have opposite phases.

In perhaps the most striking experiment of the paper, Madan *et al.* illuminated an aperture in a metallic film to produce waves called surface plasmon polaritons (SPPs), which are, essentially, light fields bound to the metal surface (Fig. 1). The electron beam passed through and interacted with these SPPs and with fields on the opposite side of the film. This created a spiral-shaped interference pattern that encoded the relative phases of the light fields at each position on the film, and therefore contained holographic information. When the authors tilted the film in the electron beam, the spiral became distorted in a way that reflected the different propagation directions of the SPPs — in much the same way as the pitch of an ambulance siren sounds different depending on whether the vehicle is driving towards or away from you.

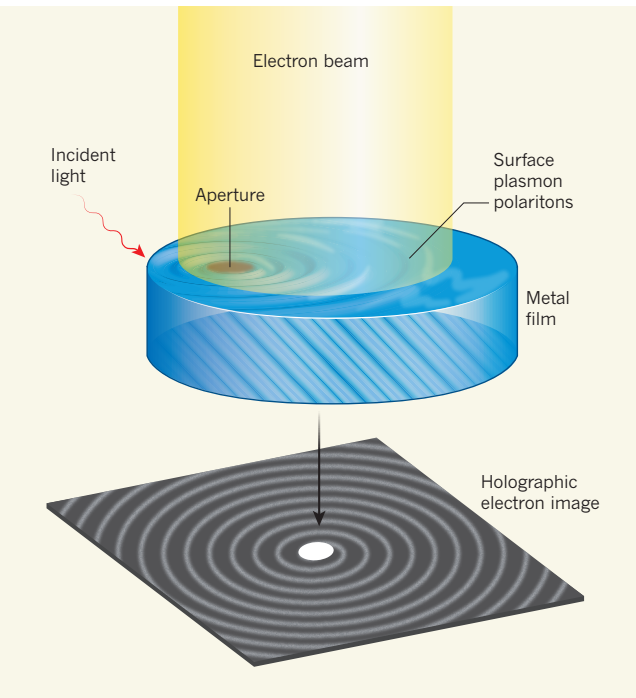

Figure 1 | Imaging of electron–light interference. Madan *et al.*[2] report new types of hologram produced by the scattering of electrons by light fields. In one of the experiments, light irradiates a metal film that contains an aperture, to produce waves called surface plasmon polaritons — light fields bound to the metal surface. A different light-field pattern (illustrated by stripes) is produced on the other side of the film. When an electron beam passes through the film, it subsequently interacts with the fields on both sides, producing a spiral interference pattern. This pattern encodes the relative phases (the patterns of peaks and troughs) of the light fields at each position on the film, and therefore contains holographic information.

Similar interference patterns have previously been observed[8] in experiments in which light fields lead to the emission of electrons from surfaces, but there are key conceptual differences between those experiments and the current work. Specifically, some of the holograms in the present study arise from the quantum-mechanical interference of electron beams, rather than from the interference of crossed light waves. Notably, in Madan and colleagues' study, the electrons, effectively, mediate interference between light waves that do not overlap. In other words, optical phase information is imprinted on an electron in one place and then 'read out' by a second light field at a different location.

The ability to use electrons to transport optical phase information potentially opens up a variety of applications in electron microscopy and beyond. For example, it should be possible to use such phase information to measure the optical response of single or coupled quantum light emitters embedded in solids, such as individual atoms, molecules or point defects in a

crystal. Getting electrons to interact with more-complicated laser-pulse sequences than in the current experiment, and with multiple colours of light, might facilitate entirely new forms of electron spectroscopy. Combined with methods for the light-induced temporal structuring of electron beams[9–11], Madan and colleagues' holographic approaches could enable the behaviour of materials to be studied on shorter timescales than that of a single wave cycle of light (the attosecond scale), and with the spatial resolution of an electron microscope.

It remains to be seen whether more-ambitious applications of the new findings will materialize, in which electron beams are used as part of quantum communication systems, or even in quantum computation. Such technologies would probably require the controlled coupling or quantum correlation of multiple free electrons with each other, neither of which has been achieved so far. In the meantime, Madan and colleagues' work represents exciting progress in the manipulation of electrons by light. ■

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COMPUTATIONAL CHEMISTRY

Holistic models of reaction selectivity

Computational models that predict the selectivity of reactions are typically accurate for only a specific reaction type and a narrow range of reaction components. A more general model has now been reported. SEE ARTICLE P.343

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Selectivity is a linchpin of chemical synthesis — if a synthetic reaction is not selective, it cannot give a good yield of the desired product, and will require tedious purification processes. Chemists have therefore long sought ways of predicting the selectivity of chemical reactions. Computational models can be constructed, but their development is laborious, and they are usually specific to a particular reaction type. On page 343, Reid and Sigman[1] now show that a selectivity model can be built in a semi-automated way and generalized over a range of reactions.

Chemical selectivity comes in many flavours, but it is especially difficult to achieve enantioselectivity, which depends on a property called chirality. Molecules are said to be chiral if they come as two mirror-image forms — enantiomers — that have many identical properties, but can differ in certain important aspects. A good analogy is with hands: a person's right and left hands have the same length, colour and mass, but only one fits into a right-handed glove.

Many biological targets for pharmaceuticals look like right-handed gloves to molecules — only one enantiomer of a molecule will fit into them. For this reason, pharmaceuticals should be synthesized as one enantiomer only; the other form might even be toxic. Asymmetrical catalysts are used to influence synthetic chemical reactions to form only one enantiomer of the product. Nature's asymmetrical catalysts are enzymes, which produce single enantiomers of biomolecules efficiently and with exquisite selectivity. Enzymes can also be used as catalysts for synthetic chemistry, but they generally have a limited range of substrates and can produce only one of the two possible enantiomers of a product.

Modern synthetic catalysts challenge the efficiency of enzymes, and can often be made as mirror-image forms that each produce a different enantiomer of a desired molecule. To support the development of new catalysts, chemists use models to understand and predict the enantioselectivity of catalytic reactions[2,3]. These range in complexity from simple models of the catalyst drawn on paper, onto which a molecular model of the substrate is superimposed to estimate the best fit, to quantum-mechanical calculations that describe an entire reaction path.

"It is highly encouraging to see that holistic reaction models can be produced by using a wide training set."

A direct predecessor of Reid and Sigman's modelling work is a computational approach called quantitative structure–selectivity relationships (QSSR), in which a correlation is sought between the properties of reaction components and the observed selectivity. The relevant properties can be either determined experimentally or calculated, and can include such things as molecular-bond lengths, vibrational frequencies and atomic charges. Using a semi-automated statistical approach (multiple linear regression), these properties are used to construct a model that outputs one numeric value for each reaction system being studied[3]. A result of zero means that there is no selectivity — both enantiomers are produced in equal amounts. A high value indicates a very selective system, and the sign of the numerical output (positive or negative) indicates which enantiomer is mostly produced. Opposite enantiomers of a catalyst produce opposite enantiomers of the product, and this should also be reflected in QSSR models of synthetic catalysts; this requirement is not essential for models of enzymes, however, because only one enantiomeric form of any enzyme exists in nature.

QSSR models are normally limited to a narrow set of substrates and catalysts, because the assumptions built into the machine-learning procedures are invalidated by large deviations from the molecular structures used to train the model. Reid and Sigman have taken on the challenge of making a general QSSR model, starting from an earlier model reported by Reid and colleagues[4].

Inspired by enzyme models, Reid and Sigman ignored the sign conventions usually adhered to in models of synthetic catalysis — that is, they produced a model that predicts the magnitude of enantioselectivity for a group of catalytic reactions (Fig. 1), but only for one enantiomer of the catalyst. Switching the catalyst to its mirror image will therefore not switch the sign of the output in their model, and the model cannot predict which enantiomer is produced as the major isomer. However, the major enantiomer can be predicted from the preceding work[4]. Within this framework, the authors demonstrated that one of the components of the modelled reactions could be varied to an unprecedented degree, without affecting the high accuracy of the predictions.

How can one model achieve such a wide range of accurate predictions? Part of the explanation is probably that all the reactions share a similar mechanism: a planar substrate (an imine molecule; Fig. 1) is 'gripped' from