

## QUANTUM PHYSICS

## Coherence in molecular nitrogen

The wave nature of matter is well established for isolated particles, from electrons to molecules. Now experiment reveals that even deeply buried core-shell electrons in a diatomic molecule can emit coherently.

## MARKUS ARNDT

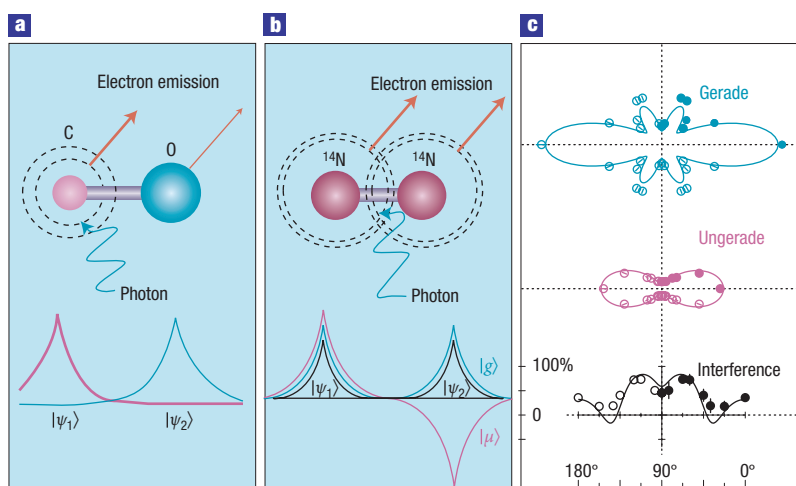
is at the Institute for Experimental Physics, University of Vienna, Boltzmannngasse 5, A-1090 Vienna, Austria.

e-mail: markus.arndt@univie.ac.at

The boundary between quantum physics and classical physics is often believed to be determined by the size of the system: small objects follow the laws of quantum mechanics; large ones should behave classically. However, in recent years several experiments have shown<sup>1</sup> that it is more appropriate to draw the line of demarcation between objects, or quantum pathways, that are either 'distinguishable' or 'indistinguishable'. This distinction is also important when it comes to the intriguing question of whether strongly bound electrons in diatomic molecules could exhibit quantum coherence and be partially delocalized over both atomic cores<sup>2</sup>. The answer — reported in *Nature* by Daniel Rolles and colleagues<sup>3</sup> — reveals the surprising physical complexity of even such a simple system as a molecule composed of only two atoms.

Electrons are certainly small, and since the early days of quantum mechanics it has been known that electrons may be 'smeared out' over rather large distances, if there is no way of distinguishing the specific position of an electron. However, the innermost electrons of most molecules are so strongly bound to the atomic cores that we would usually expect them to be highly localized on one of the atoms. The experiment performed by Rolles *et al.*<sup>3</sup> now proves the non-local character of K-shell electrons in molecular nitrogen. The authors also show that there is a partial loss of coherence through symmetry breaking when one nitrogen atom is replaced in the molecule by a heavier isotope.

Probing an electron's wave function *in situ* is a significant challenge, but photoelectron spectroscopy turns out to be a suitable tool. In molecular nitrogen, synchrotron photons with energies of about 410 eV are needed to boost the core electrons into the continuum, where, inside a sophisticated spectrometer, their properties can reveal their origin. In fact, the ionization cross-section grows dramatically for photon energies that are a few electron volts higher than the continuum threshold, and the experiments are usually performed at photon energies of about 419 eV.



**Figure 1** Photoelectron spectroscopy of diatomic molecules is reminiscent of Young's double-slit experiment. **a**, Coherent scattering can occur in a heteronuclear molecule, such as carbon monoxide. An electron, localized on a single atom, may be emitted and subsequently detected with or without being coherently scattered by the partner atom. The qualitative picture of the atomic wave functions indicates localized core electrons. **b**, Molecules composed of indistinguishable atoms, such as diatomic nitrogen, may also emit coherently from both atoms, as indicated by the two partially overlapping wave functions. The molecular superposition states  $|\mu\rangle$  and  $|g\rangle$  are formed from the indistinguishable atomic states. A nitrogen core electron has a 15% chance of being detected at the partner atom<sup>10</sup>. **c**, Data from Rolles *et al.*<sup>3</sup> show the different angular dependence of the electron emission probability for the  $|\mu\rangle$  and  $|g\rangle$  states, the interference pattern revealing the coherence of the emission. The open circles are the mirror images of the measured data points (filled circles).

This 'shape resonance' for nitrogen has been known for about three decades<sup>4</sup>. But it was only very recently that experiments achieved the resolution necessary to identify a small ground-state splitting hidden underneath it<sup>5</sup>. This was a vital step because it indicated the existence of a finite-coupling tunnelling barrier between the two cores of the molecule, which allows a partial delocalization of the electrons between the sites. The ground states of the joint system are then formed as superpositions of the individual atomic states:  $|\mu\rangle \propto |\psi_1\rangle - |\psi_2\rangle$  and  $|g\rangle \propto |\psi_1\rangle + |\psi_2\rangle$ , with 'ungerade' (odd) and 'gerade' (even) inversion symmetry. The overlap between the atomic states determines the energy splitting between the  $|\mu\rangle$  and  $|g\rangle$  state, which, for nitrogen, amounts to only 97 meV.

To an optical spectroscopist, this might seem a large value, but for electron spectroscopy it requires state-of-the-art experimentation to resolve such splitting.

Back in 1966, Cohen and Fano<sup>6</sup> discussed the role of interference in the photoelectron spectra of valence electrons. Their theme was then developed by Dehmer and Dill<sup>4</sup> into the K-shell spectroscopy of diatomic molecules. The idea behind it is sketched in Fig. 1a. When an electron is ejected from one of the two atoms in the molecule, it can reach the detector along two indistinguishable paths: either directly or by coherent scattering at the partner atom. The additional question now addressed by Rolles *et al.*<sup>3</sup> is illustrated in Fig. 1b: if the electrons are partially delocalized, is it possible to see the influence of coherent emission from both sites in the molecule?

Both the scattering and the emission process very much resemble Young's double-slit experiment. Of course, a quantitative reproduction of the experimental data requires the consideration of several fine details, such as the intricacies of the anisotropic molecular potential. The result of interference is then a characteristic angular dependence of the electron emission probability with respect to the alignment of the molecular axis. Even the determination of the molecular orientation is far from trivial, given that all molecules are randomly oriented and rapidly rotating in the gas phase.

Luckily, about a decade ago, new spectrometric methods were developed<sup>7–9</sup> such that the number, energy and momentum of the ejected electrons can be correlated with both the polarization of the ionizing photons as well as with the energy and momentum vector of all of the remaining fragments after ionization. From these data, the molecular orientation can be determined for each detected emission event.

With such spectrometers to hand, Rolles *et al.*<sup>3</sup> could finally settle the question of electron non-locality: the angular distributions in Fig. 1c clearly show the coherent nature of the core electron emission. It is important to emphasize that the

authors were able to selectively read out the angular distributions of the gerade and the ungerade superposition state, which is necessary to avoid cancelling out the interference.

There is a further twist to this experiment. Rolles *et al.* also studied the electron emission pattern when one of the two nitrogen atoms was substituted by its more massive brother, <sup>15</sup>N. Mass- and spin-dependent effects are known to be rather small in nitrogen and the Born–Oppenheimer rule does not allow any direct effect on the electrons. But, from a fundamental point of view, the substitution might be expected to influence the core electrons because the symmetry between the two potential centres is now broken. And indeed, the photoelectron spectra of <sup>14,15</sup>N, when normalized to that of <sup>14,14</sup>N and compared with <sup>15,15</sup>N, reveal their reduced coherence. The spectra are modified at the level of about only one percent, as expected, but with a statistical significance of a few standard deviations.

Nitrogen is a fortunate choice for observing the influence of isotope substitution on the coherence in photoelectron spectra. It turns out that the effect is too small to be observed with either valence or core-shell electrons in any other molecule studied so far. It is surprising how many subtle quantum details there are still to learn about a seemingly simple diatomic molecule — one that we inhale by the mole every few seconds.

## REFERENCES

1. Arndt, M., Hornberger, K. & Zeilinger, A. *Phys. World* **18**, 35–40 (March 2005).
2. Pavlychev, A. A. *et al. Phys. Rev. Lett.* **81**, 3623–3626 (1998).
3. Rolles, D. *et al. Nature* **437**, 707–710 (2005).
4. Dehmer, J. L. & Dill, D. *Phys. Rev. Lett.* **35**, 213–215 (1975).
5. Hergenbahn, U., Kugeler, O., Rüdell, A., Rennie, E. E. & Bradshaw, A. M. *J. Phys. Chem. A* **105**, 5704–5708 (2001).
6. Cohen, H. D. & Fano, U. *Phys. Rev.* **150**, 30–33 (1966).
7. Shigemasa, E., Adachi, J., Oura, M. & Yagishita, A. *Phys. Rev. Lett.* **74**, 359–362 (1995).
8. Heiser, F. *et al. Phys. Rev. Lett.* **79**, 2435–2437 (1997).
9. Becker, U., Geßner, O. & Rüdell, A. *J. Electron Spectrosc. Relat. Phenom.* **108**, 189–201 (2000).
10. Kosugi, N. *J. Electron Spectrosc. Relat. Phenom.* **137–140**, 335–343 (2004).