Cold encounters: Electrons and molecules

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Cold collisions give a special insight into quantum dynamics, since cold encounters emphasise the coherent wave nature of matter. In cold collisions particles may pass ghost-like through each other or pursue a superposition of energetically forbidden trajectories, in a manner alien to a classical vision of natural phenomena. Cold electron collisions have the additional attraction that they occur in the natural world, in planetary atmospheres and in the interstellar medium, as well as in industrially important plasmas for device fabrication.

A cold collision is one in which the de Broglie wavelength of the projectile is much greater than the physical dimensions of the target species. Two parallel experimental developments have aroused strong interest in cold collisions. The first is the achievement of Bose-Einstein condensation, which depends for its success on cold collisions, and to a Rb atom at a temperature of 500 μK. When cold electrons encounter molecules, they can be elastically scattered, they can excite rotation and vibration in the targets or they can cause the formation of negative ion products, a process called dissociative attachment (DA).

How cold is cold?
The de Broglie wavelength of an electron with kinetic energy of 10 meV (1 meV = 8.0655 cm⁻¹ = 96.485 J mol⁻¹) is 12.3 nm, equivalent, for comparison with atom-atom collisions, to a Rb atom at a temperature of 500 μK. When cold electrons encounter molecules, they can be elastically scattered, they can excite rotation and vibration in the targets or they can cause the formation of negative ion products, a process called dissociative attachment (DA).

Experiments
Two types of experiment have been developed. The first are those that form cold electrons or Rydberg atoms in situ with a target gas to study exclusively DA [3,4,5,7]. The exquisite precision of recent DA measurements is illustrated by data in [8], involving CH₃I + electron → I⁻ + CH₃, showing how the cross-section for I⁻ production is strongly affected by vibrational motion in CH₃I through “vibrational Feshbach resonance”.

The second type of experiment uses electron beams and involve elastic and inelastic scattering, as well as DA. The apparatus with which the great majority of these data have been acquired is shown in Figure 1 [6]. Electrons are formed by the threshold photoionisation of Ar at 15.76 eV, using synchrotron radiation from the ASTRID storage ring, University of Aarhus. A beam of electrons, with a resolution which may be better than 1 meV, passes through gas at room temperature, and the attenuation of the beam yields the scattering cross-section. A great variety of species has been studied with this apparatus, ranging from the simplest diatomics, H₂, N₂, O₂ to more complex molecules such as benzene, hexafluorobenzene and still larger species such as naphthalene or anthracene. These studies have revealed a number of fascinating quantum scattering phenomena, some known or strongly suspected from theory, such as powerful rotational excitation in polar molecules with cross-sections of several thousand Å², others unknown and which remain largely unexplained.

Understanding the data
How does the incoming electron appear to the target molecule, and how does the molecule appear to the electron? Because of the wave nature of the cold electron, it is spread out in space and the incoming wave explores a superposition of paths, rather than a well-defined classical path. Each path within this superposition may be accorded a collisional angular momentum, which is quantized with respect to the molecular target at the “scattering centre”. Moreover on the time-scale of encounters, even at meV energies, the target molecule has no time to rotate and presents a single face to the incoming electron. The “head-on” component of the electron trajectory is called the “s-wave”, with angular momentum zero, with “p-waves” for angular momentum of unity and so on. Let us say for example that only the s-wave is scattered: the steady state angular distribution of scattered electrons will then be spherically symmetrical about the target. If a p-wave is scattered, then the electron will by contrast show backward-forward scattering asymmetry.

The beauty of cold collision studies is that only very few of these so-called “partial waves” are involved in scattering, in fact only s- and p-. As these waves are scattered, they undergo energy dependent phase shifts, which quantum theory shows may be simply related to scattering cross-sections. Expressions for cross-sections include the coherent superposition of scattered s- and p-waves, for example for backward-scattering. Predictions about the relative amount of backward and forward scattering, for example, may be compared with experiment and this style of analysis gives considerable insight into the nature of cold collisions.

The point of view of the electron
How does the molecular target appear to the electron beam? Imagine yourself sitting on the electron wave as you accelerate towards the molecule. In order to understand your fate, you can think of yourself as refracted through the target with a refractive index of more than or less than unity. The former case corresponds to a weak interaction and the target appears closer than it truly is. The system is said to possess a “positive scattering length”. If for a different target the
field is stronger, the target may appear further away, equivalent to a refractive index of less than unity, and the system possesses a negative scattering length. If the field is very strong, there may be a bound state within the electron-molecule potential well, and the scattering length becomes positive again. The latter can lead to dissociative attachment.

As the electron energy tends to zero, so the cross-section tends to the surface area of a sphere of radius the scattering length, A, that is, 4\pi A^2. The sign of the scattering length is however crucial to understanding the nature of the collision. You may be deflected with low cross-section (small positive A), be projected into a virtual state (large negative A) or you may attach and perhaps dissociate the molecule (large positive A).

The response of the target: symmetry
A further powerful concept, in addition to that of partial waves, involves the symmetry of the molecular target. Both DA and virtual state scattering involve an initial step of attachment, however fleeting, of the electron to the target molecule. A low energy electron will attempt to attach into the "lowest unoccupied molecular orbital" or LUMO, whose symmetry is dictated by that of the host molecule, such as a hexagon for benzene or a football for \( \text{CCl}_4 \). The impinging electron is also subject to this symmetry, and the incoming wave must be able to fit into the LUMO. For example, spherical s-waves fit snugly into the spherical LUMO of \( \text{CCl}_4 \), whereas the water-wings form of a p-wave does not.

In Figure 2, we show data for \( \text{CO}_2 \), which shows strong scattering at low energy [9]. However, weak scattering is expected; for example, the cross-section for \( \text{N}_2 \) at 10 meV is only \( \sim 3 \times 10^{-20} \text{m}^2 \), nearly 50 times lower than \( \text{CO}_2 \). The strange behaviour of \( \text{CO}_2 \), which we have found in a number of other molecules, is due to virtual state scattering. This process may be understood in terms of lifetimes of scattering states.

Lifetimes in scattering
How sticky are electron-molecule collisions? That is, if you were to time the passage of an electron over some distance, what difference in travel time would result if the electron experienced a scattering process or if it moved unimpeded? Theory shows that the lifetime of a collision complex is equal to twice the rate of change of the phase of the electron wave with collision energy, in atomic units. This rate of change may be obtained by suitable fitting of the data in figure 2, resulting in a lifetime of \( \text{CO}_2 \) at 10 meV impact energy of \( 8.48 \pm 0.1 \times 10^{-15} \) seconds. But how can this be? An s-wave is attempting to attach to \( \text{CO}_2 \). The LUMO of \( \text{CO}_2 \) is however of p-like symmetry: the overlap is zero. But let us say that the molecule borrows some time from the classically inaccessible quantum world, in a manner restricted by the Heisenberg relationship \( \Delta E \Delta t \geq h/2\pi \). In this borrowed time, the system may explore paths in which the molecule is "virtually bent", where virtual implies something happening in borrowed time. As the molecule virtually bends, the p-like orbital splits into two components, one of which is of spherical symmetry and can happily accommodate an s-wave. When the interaction is over, the borrowed time is returned—but not all. The lifetime of \( \sim 8.5 \times 10^{-15} \) seconds may then be seen as a remnant of the borrowed time.

Molecules may also be transparent to electrons, rather than present a large cross-section. For example, at 90 meV impact energy, electrons pass almost unimpeded through \( \text{CF}_4 \), in the so-called Ramsauer-Townsend effect. It is as if the molecule were not present and you might very reasonably conclude: no scattering, no phase shift of the electron matter wave, no effect at all. However, this is not so. The scattering state is found rather to have a negative lifetime of \( 900 \pm 60 \times 10^{-18} \) seconds. Thus the electron spends less time than the molecular mass would suggest, so as to produce the Ramsauer-Townsend effect. The LUMO of \( \text{CO}_2 \) is however of p-like symmetry: the overlap is zero. But let us say that the molecule borrows some time from the classically inaccessible quantum world, in a manner restricted by the Heisenberg relationship \( \Delta E \Delta t \geq h/2\pi \). In this borrowed time, the system may explore paths in which the molecule is "virtually bent", where virtual implies something happening in borrowed time. As the molecule virtually bends, the p-like orbital splits into two components, one of which is of spherical symmetry and can happily accommodate an s-wave. When the interaction is over, the borrowed time is returned—but not all. The lifetime of \( \sim 8.5 \times 10^{-15} \) seconds may then be seen as a remnant of the borrowed time.

Conclusions
We set out by suggesting that the study of cold collisions may help us to understand the nature of quantum mechanics, and perhaps the strange phenomena of quantum mechanics.

References