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Insights from the classical atom

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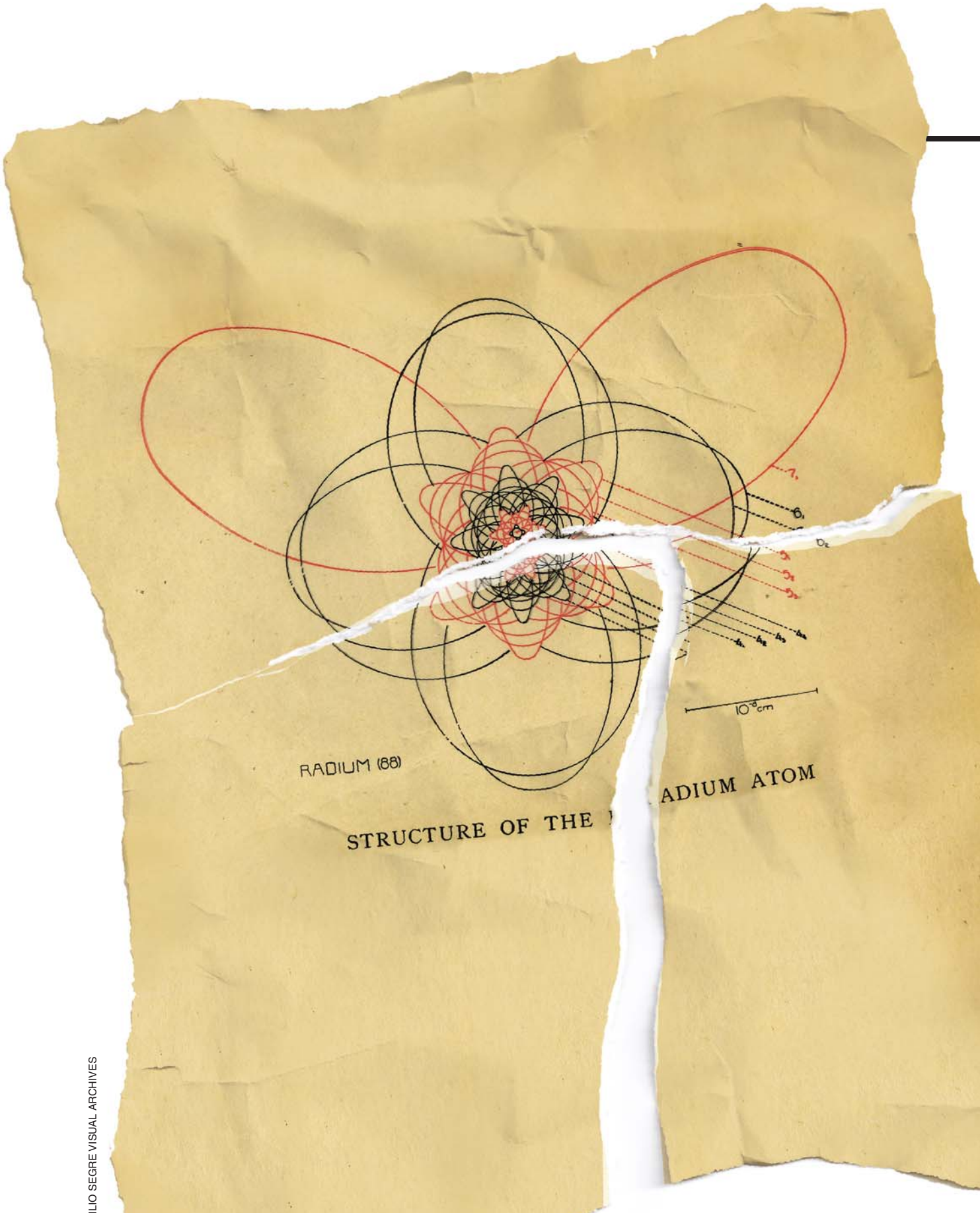

STRUCTURE OF THE ADIUM ATOM

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CLASSICAL ATOM

Petar Grujić and Nenad Simonović

Decades after the 1920s rise of quantum mechanics, the classical mechanical framework remained a useful lens through which to examine ionization, scattering, and other atomic processes.

Richard Feynman once wrote that the concept of the atomic structure of the material world was the most fertile idea we inherited from antiquity. But although the so-called atomic hypothesis traces its beginnings to the fifth century BC (see box 1), it was only a century ago, in 1911, that the atom secured its place as the cornerstone of the modern physical sciences. That year marked two important advances in our understanding of the microscopic world. First, from the observation that α particles were deflected as they passed through a thin gold foil, Ernest Rutherford arrived at the planetary model of the atom, in which electrons orbit a massive nucleus. Second, he evaluated the angle-differential cross section for the deflection of the α particles.[1]

Rutherford's formula was purely classical—he treated atomic particles as having trajectories influenced by Coulomb forces—yet it proved remarkably accurate. An identical expression can be derived quantum mechanically by calculating the scattering amplitude due to Coulomb interaction in the limit of weak scattering, where the first Born approximation holds (see box 2).

The success of Rutherford's calculations, however, was soon overshadowed by the advent of quantum mechanics (QM), which triumphed in describing atomic and subatomic processes. Deemed generally inadequate, the classical approach was neglected until 1953, when Gregory Wannier, then at Bell Labs, used classical mechanics to derive a law describing near-threshold atom ionization due to electron impact.[2] In the decades that followed, various efforts from an assortment of groups demonstrated the enduring capacity of classical mechanics to elucidate the structure and interactions of atoms.

The classical potentials

Interactions between atomic particles fall mainly into three classes: long-range potentials of the form $V(r) = \beta/r$; medium-range potentials of the form $V(r) = \beta/r^n$, $n > 1$; and short-range potentials of the form $V(r) = \gamma r^n e^{-\alpha r}$, $\alpha > 0$. Here, r is the interparticle distance. The long- and medium-range potentials—the power-law interactions—derive from the concept of fluxes and force lines. Considered classical interactions, they include the Coulomb potential, $n = 1$, and the monopole–dipole potential, $n = 2$. (The harmonic oscillator potential, $n = -2$, is another noteworthy classical interaction.) The short-range, exponential potentials are typically quantum mechanical and based on the notion of exchange of intermediary bosons, as in the case of the strong interaction.

With the advent of QM came rigorous criteria for determining when the classical approach is justifiable. Based on the underlying physical ontology of wave mechanics, the classical approximation was shown to be applicable when the rate of change of the reduced de Broglie wavelength $\lambda\!\!\!^{-} = \hbar/p$ is small—that is, when $d\lambda\!\!\!^{-}/dr \ll 1$. For a binary collision, the most common type of atomic collision, the condition reduces to $r^{n-2} \ll 8\mu|\beta|/(\hbar^2 n^2)$ for power-law potentials, provided $\beta < 0$ and the energy of the system is small. Here, μ is the reduced mass.

In the case of the Coulomb interaction, for which $n = 1$, the criterion becomes $r \gg \hbar^2/(8\mu|\beta|)$. The classical approximation is therefore applicable for asymptotically large interparticle distances, a result that turns out to be of particular importance for modeling near-threshold processes. For the monopole–dipole interaction, where $n = 2$, the condition is fulfilled as long as the interaction term is strong

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Box 1. A brief history of the atom

The concept of the atom arose in the fifth century BC in the Abderian region of northern Greece. Presumably conceived by Leucippus, predecessor of the famed philosopher Democritus, the atomic hypothesis was the Abderian response to an existential puzzle known as the Eleatic challenge: In short, What can explain the plurality of things found in nature?

Leucippus's idea, that indivisible particles constitute the backdrop of the physical world, was further pursued by Epicurus, who identified a number of empirical phenomena that seemed to corroborate the idea of microscopic particles moving chaotically in the void. The most popular exposition of the atomic concept, later extended by Epicurus, was authored by Lucretius in the first century BC:[17]

> It clearly follows that no rest is given to the atoms in their course through the depths of space. Driven along in an incessant but variable movement, some of them bounce far apart after a collision, while others recoil only a short distance from the impact. . . . Then those small compound bodies that are least removed from the impetus of the atoms are set in motion by the impacts of their invisible blows and in turn cannon against slightly larger bodies. So the movement mounts up from the atoms and gradually emerges to the level of our senses, so that those bodies are in motion that we see in sunbeams, moved by blows that remain invisible.

As fertile as it was, the atomic hypothesis suffered from a major deficiency: Its authors happened to be atheists. Subsequent generations were reluctant to accept the atom, and the concept remained buried in religious animosity for nearly two millennia. Plato never mentions Democritus, and the Abderian thinker, arguably as great a mind as Plato and Aristotle, was relegated to obscurity until the late Renaissance. (The gods were kinder to Democritus than were his fellow mortals and allotted him 93 years of life—or 109, according to some authors.)

The atomic hypothesis was revived by a number of European scientists, including Pierre Gassendi in the 17th century and John Dalton in the 18th. Atoms became the subjects of chemistry and the basis for statistical models of gases. In the late 19th century, with Jean Perrin's observation of Brownian motion in a colloidal suspension, the concept of the atom returned at long last to the realm of physics.

enough—specifically, when $|\beta| \gg \hbar^2/2\mu$. For $n > 2$, the classical approximation is valid only when the particles are close, approximately within one Bohr radius of each other. The short-range, exponential potentials are essentially beyond the reach of classical approaches.

The ontological and epistemological bridge between the classical and quantum mechanical domains is embodied in Niels Bohr's correspondence principle. It stipulates that semiclassical results—specifically, those based on Bohr's old quantum theory, in which orbital electrons have quantized energy but otherwise obey Newton's laws of motion—should converge with quantum mechanical ones in the limit of large quantum number. For large principal quantum number N and reasonably large angular momentum quantum number l, one may thus speak of an electron as having a trajectory. It was on that principle that Louis de Broglie posited the wave nature of particles.

But are there circumstances in which semiclassical and quantum mechanical results coincide for all values of quantum numbers? Provided one ignores the spin variable—an essentially quantum mechanical quantity—the answer is yes: for power-law potentials having $n = 1$ or $n = -2$. That result is among what's known as the correspondence identities,[3] and considering that $n = 1$ and $n = -2$ potentials describe arguably the two most important interactions in physics—the Coulomb and harmonic-oscillator interactions—its methodological and historical significance cannot be overstated. It explains the considerable success of QM's predecessors—Max Planck's quantum physics and Bohr's old quantum theory. And one can only guess to what extent the discovery of the nucleus might have been delayed had it not been for the coincidence of classical and quantum mechanical cross sections for Coulomb interactions. Alternatively, one might argue that QM would have appeared sooner had shortcomings in the old quantum theory not been masked by the special properties of $n = 1$ and $n = -2$ potentials. The correspondence identities also help to explain, albeit implicitly, why classical mechanics successfully describes so many physical phenomena, particularly near-threshold processes.

Near-threshold fragmentation

In 1953 a seminal paper on classical atomic physics made its debut. Written by Wannier, it presents a general classical framework for describing near-threshold fragmentation of atomic systems.[2] Near-threshold modeling remains arguably the most fruitful application of the classical approach; Wannier's paper opened an entirely new field spanning theoretical physics, atomic physics, and even celestial mechanics. Interestingly, Wannier, a solid-state physicist, published only two papers in atomic physics in his career. His brief excursion into the realm of atoms, however, turned out to be remarkably fertile.

Without specifying any particular system or type of interaction, Wannier's model assumes that a violent collision can be described as having three stages, as depicted in figure 1. Leading up to the collision, reactants (A and B in the figure) approach each other along a path known as the entrance channel. Postcollision, the products (C, D, and E) escape via the exit channel. The collision itself proceeds via an intermediate compound state, in which all constituents are strongly coupled.

The centerpiece of Wannier's model is a quasi-ergodic hypothesis: Particle trajectories inside the compound state are sufficiently irregular, almost chaotic in fact, that the particles have no favored path of escape. In other words, there is no singularity in the relevant distribution functions prior to particles emerging from the compound state and into the exit channel.[4]

In a system with only short-range interactions, particles outside the compound state move practically freely, and their trajectories can't be computed classically. In a system with long-range and medium-range interactions, however, there exists a quasi-asymptotic region beyond the compound state, in which interparticle forces subside gradually. Thus classical treatment of, say, near-threshold ionization is possible.

Adopting Wannier's model, one may consider without loss of generality an ionization in which the energy E_{im} of an impinging electron is exactly equal to the ionization energy E_{thr} of a target atom. The total energy, $E = E_{im} - E_{thr}$, is zero. Both electrons in a single

ionization—or $n+1$ electrons in an n-fold ionization—must escape the compound state with equal shares of energy if they are to both reach the asymptotic regime. The overall potential of the system should be minimal, which in turn requires a maximally symmetric final configuration. In the case of single ionization, that means the two electrons escape in opposite directions along the same straight line. In a double ionization, the three electrons' escape trajectories lie at 120° angles. The maximally symmetric, zero-energy trajectories are known as the leading, or scaling, configuration. One can show that since the number of leading configurations is smaller than the number of all possible exit-channel trajectories, the probability of ionization must be zero at the energy threshold.

As the total energy of the system increases from zero, the cross section becomes finite. Wannier describes such near-threshold behavior in terms of the energy dependence of the fragmentation cross section σ in the zero-energy limit. In most cases the threshold law assumes the simple form $\sigma \sim E^{\kappa}$, $E \to +0$, and the problem reduces to evaluating the exponent κ, which need not be a real number.

In deriving his threshold law, Wannier made use of two important points: First, the rate of change of the phase space of potential escape trajectories can be encompassed in a single variable; second, scaling laws may be applied in deriving classical solutions. The former greatly simplifies numerical integration, and the latter facilitates analytical calculations. For example, if $\mathbf{r}_i(t)$ is a solution for a coulombic system with energy E, then $\theta\mathbf{r}_i(\theta^{3/2}t)$ is a solution for one with energy $\theta^{-1}E$.

Wannier found that in the asymptotic zone, an electron moves along the leading trajectory according to $r^3 = (9e^2Z'/2m_e)t^2$, where Z' is the effective charge of the nucleus, m_e is the electron mass, and e is the electric charge. Notably, the particle trajectory is independent of energy when the energy is small. Readers familiar with the standard cosmological model will recognize that the $t^{2/3}$ dependence also describes the evolution of the cosmic scale factor. Since coulombic and Newtonian forces follow the same dependence on interaction distance, atomic and celestial systems have much in common. As a result, the Wannier model contains the essential features of the Big Bang concept. Indeed, Georges Lemaître, author of a precursor to the Big Bang theory, made extensive use of the concept of a "cosmic atom" in his model of an expanding universe.[5]

Formally, describing the near-threshold behavior of any fragmentation process amounts to determining how the phase space of potential escape trajectories shrinks as $E \to +0$. By considering small deviations in trajectory from the leading configuration, Wannier obtained the threshold exponent κ for a three-body coulombic system:

$$\kappa = \frac{3}{4}\sqrt{1 + \frac{16}{9}\frac{1+2m}{1+q/4}} - \frac{1}{4}, \quad q = \frac{q_{2,3}}{q_1}, \quad m = \frac{m_{2,3}}{m_1}$$

where m_i and q_i are the mass and charge of the ith particle, respectively, and particles 2 and 3 are identical.[6] For $q = -1$ and $m_1 \gg m_2$, which corresponds to the ionization of hydrogen by electron impact, the formula returns $\kappa = 1.1269$.

Note, however, that when $q = -4$, κ diverges. At first, few people paid attention to that possibility, in

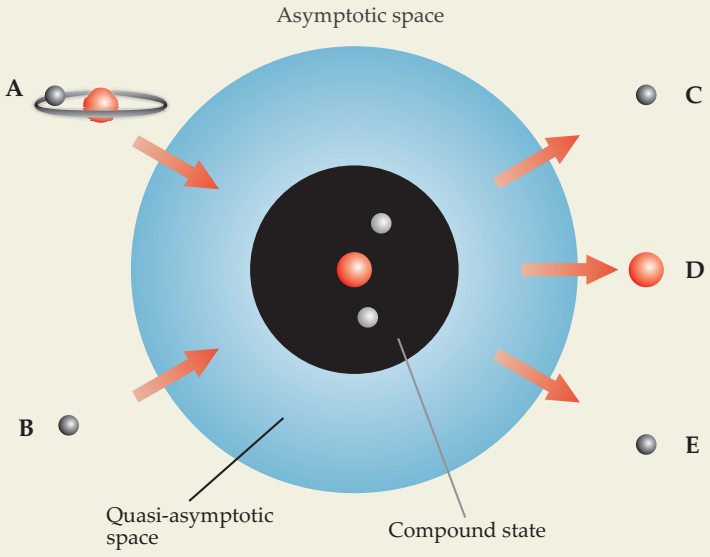

Figure 1. Near-threshold collision can be thought of as a three-step process. Reactant systems (A and B) approach and then thoroughly interact in a strongly coupled compound state. If the constituent particles acquire enough kinetic energy, they overcome the attractive Coulomb forces that prevail in the quasi-asymptotic region and escape into asymptotic space as products (C, D, and E). This particular illustration depicts the ionization of hydrogen by an electron.

Box 2. Where classical and quantum converge

Ernest Rutherford's classical formula describing the cross section σ for deflection of α particles by gold-foil atoms reads

$$\frac{d\sigma}{d\Omega} = F(E)\csc^4\theta/2$$

where θ is the deflection angle, $d\Omega$ is a differential solid angle, and $F(E)$ depends essentially on the impact energy E, charge, and atomic numbers of the particles.[18] The same expression is derived quantum mechanically by calculating the scattering amplitude for the Coulomb interaction within the first Born approximation. For collisions between identical particles, the quantum mechanical solution in the center-of-mass frame is

$$\frac{d\sigma}{d\Omega} = F(E)[\csc^4\theta/2 + \sec^4\theta/2 + 8\csc^2\theta\cos(\kappa\ln\tan^2\theta/2)]$$

where the parameter κ is inversely proportional to the particles' mutual velocity. The last term arises due to quantum mechanical exchange and cannot be obtained via classical theory. However, it vanishes in the limit of small velocity, in which case the cosine term oscillates rapidly and cancels over observable length scales. Then, if one of the particles is fixed in the laboratory frame, the scattering formula reduces to that of Rutherford, after the proper coordinate transformations.

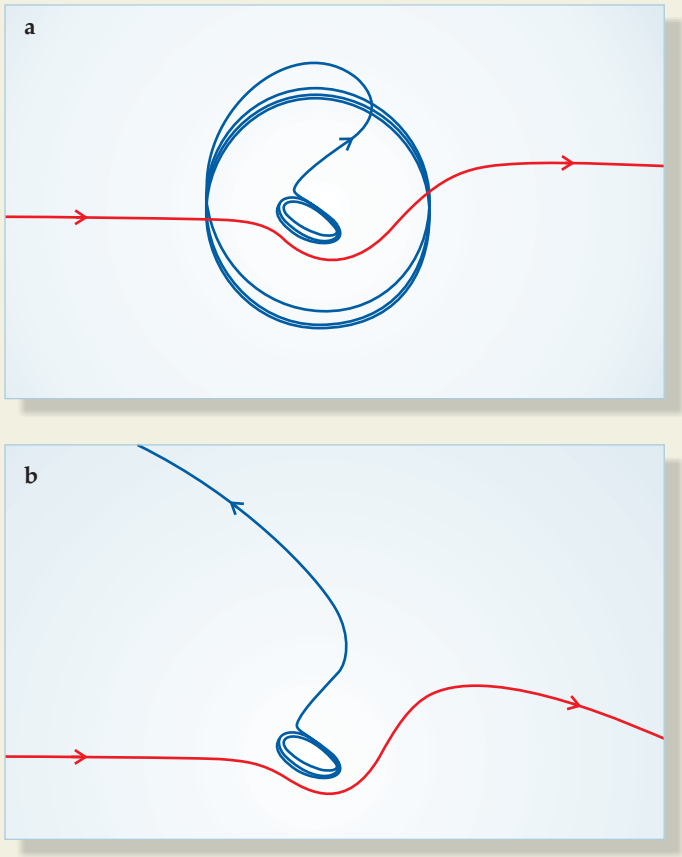

Figure 2. Classically calculated trajectories of a hydrogen-atom electron (blue) and an impinging electron (red). In **(a)**, the incoming electron excites the H atom; in **(b)**, the atom is ionized.

part because such systems are both experimentally and theoretically cumbersome, even in the simplest possible case: $Be^{4+} + Be^{3+} \rightarrow e + 2Be^{4+}$. After carrying out numerical investigations of several model systems,[6] we arrived at a threshold law of the form

$$\sigma \sim e^{-\lambda/\sqrt{E}}$$

with $\lambda = 0.33$ if E is in atomic units. That singular case was discussed in the broader context of near-threshold phenomena in reference 4. In particular, limitations of the Wannier approach were pointed out, and theoreticians were urged to contrast its predictions with those of QM. Subsequent analytical calculations largely confirmed the classical numerical results and further developed the subject in the process.[7]

Expressions for the near-threshold behavior of the fragmentation cross section prove to be of considerable value. For instance, they facilitate precise estimation of energy thresholds, which are difficult to determine experimentally. Other features of fragmentational collisions, including the final energy distribution, mutual-angle behavior, and angular momentum distribution, are also important. In the decades following the introduction of Wannier's model, a variety of classical approaches were developed to model various aspects of atomic collisions. We highlight two that might be considered as occupying opposite ends of a spectrum: classical-trajectory Monte Carlo (CTMC), an ab initio semiclassical approach developed by Ian Percival and coworkers at the University of Stirling in the UK; and a purely classical, phenomenological approach conceived by a Warsaw University group led by Michał Gryziński.

The Stirling school

In the late 1960s, Percival and coworkers developed a versatile computer code, classical-trajectory Monte Carlo, for modeling three-body systems of charged particles, two of which are identical.[8] (For an instructive review of classical simulations before 1968, see reference 9.) Eschewing Wannier's reliance on a quasi-ergodic compound state, Percival's approach was to calculate the full-collision particle trajectories, including in the strong interaction region where the classical approximation need not be legitimate. Given the system energy, CTMC finds the probability of escape based on a statistically large sampling of initial conditions. In that sense, it preserves the probabilistic nature of the quantum mechanical formalism.

In Percival's model, the target atomic system retains as many quantum attributes as possible. Atoms are treated as having Keplerian electron orbits endowed with bound-state energies and variable orbital angular momenta, as prescribed by old quantum theory. The electrons exhibit a classical velocity distribution that coincides with the quantum mechanical one—another consequence of the correspondence identities.[8] Basically, the quantum mechanical nature of the bound systems is duly recognized but incorporated into a more transparent, albeit approximate, classical picture. Aside from the classical approximation, no further dynamical approximations are made.

With proper modifications, CTMC can be used to numerically calculate near-threshold ionization, excitation, and other small energy processes (see figure 2). And although it was originally devised for coulombic systems, various researchers modified it for other types of interactions. One version of the model was used to simulate detachment of an electron from H^- ($e + H^- \rightarrow e + H + e$), the subject of much classical and quantum mechanical investigation.[10] The complete analytical description of the process remains elusive, and theorists have instead resorted to approximating the process with electron–atom and electron–negative ion model interaction potentials. Figure 3 contrasts some of the theoretical results with experiments and with results obtained via CTMC.

Qualitatively, the CTMC results compare favorably with the theoretical ones, except that they predict a threshold energy about 1 eV higher than the experiments indicate. The shift turns out to be a consequence of Coulomb repulsion, which creates a potential barrier in the entrance channel of the impinging electron. In a quantum mechanical system, the barrier is overcome by quantum tunneling, but no such phenomenon exists in classical mechanics. Interestingly, with the proper choice of the three-body potential function, it is also possible to use CTMC to evaluate the cross section for $e + H^- \rightarrow e + H + e \rightarrow H^- + e$, in

which an impinging electron substitutes a loosely attached H^- electron. That cross section turns out to be exceedingly small.

The Warsaw school

In contrast to the Stirling school, Gryziński and his colleagues modeled atomic collisions according to quantum mechanical phenomenology.[11] The atom is treated as a deterministic Newtonian dynamic system and the quantum mechanical formalism is considered redundant, but quantum mechanical observations are taken into account. For example, in Gryziński's model of the H atom, the bound electron has zero orbital angular momentum: Instead of tracing a circular or elliptical orbit, it oscillates along a free-fall trajectory that ends at the nucleus. (Elaborations on the free-fall model can account for electron spin in the form of a physical dipole, which results in a Lorentz force that prevents the electron from actually penetrating the nucleus.) The free-falling electron gives rise to a time-dependent interaction potential for distant atoms:

$$V(\mathbf{r},t) = [Q_m(\mathbf{r})/r^{m+1}] + [Q_n{}^{\omega}(\mathbf{r})/r^{n+1}]\sin(\omega t),$$

where Q_m and Q_n denote the leading electric multipoles and their Fourier components. The time-dependent term captures the statistical nature of the real atomic structure. From the 1960s on, Gryziński and colleagues made prolific use of the free-fall model, investigating the structural and collisional properties of an assortment of atoms and molecules. (See figure 4.)

After some early success and an initially favorable reception from the atomic-physics community, questions arose as to the reliability and ideological soundness of the Warsaw school's approach. Since both classical and semiclassical approaches were generally viewed as dissident, objections were to be expected. More condemning was the criticism from the semiclassical community, which gradually took the position that a purely classical view of the microscopic world cannot be justified.

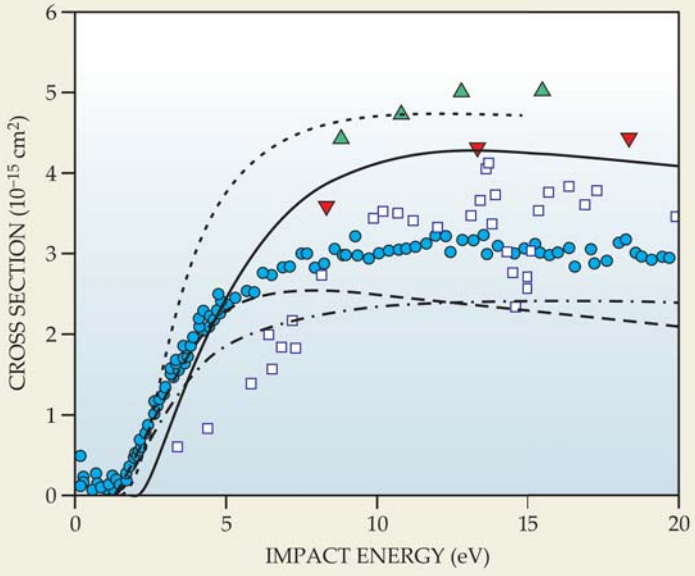

Figure 3. The cross section for detachment of a loosely bound electron from a negative hydrogen ion, $e + H^- \rightarrow e + H + e$, as computed quantum mechanically (the various dashed curves), simulated via classical-trajectory Monte Carlo (solid curve), and observed in experiments (symbols). (Adapted from ref. 10.)

The classical atom at 100

The field of classical atomic physics is too wide for us to fully capture the breadth of its influence and the extent of its community of contributors. The Saint Petersburg group led by Valentin Ostrovsky,[12] Ronald Olson's group at the Missouri University of Science and Technology,[13] and Modris Gailitis and coworkers in Riga, Latvia,[14] are just a few of the key contributors who have helped to advance theoretical and numerical aspects of classical models.

The continuing value of the classical approach is at least twofold. For one, classical calculations are often more analytically tractable than their quantum mechanical counterparts. Also, from a heuristic point of view, the classical picture provides a

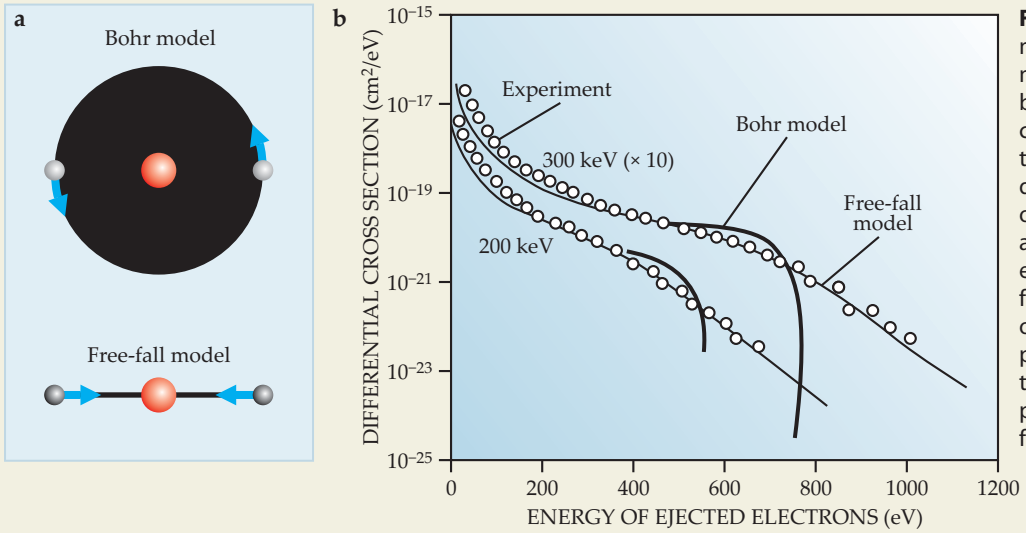

Figure 4. Two classical atomic models. (a) Whereas the Bohr model of the atom describes bound electrons as tracing circular or elliptical orbits, the so-called free-fall model describes the electrons as oscillating back and forth along radial trajectories that end at the nucleus. **(b)** The free-fall model, though unorthodox, yields favorable predictions for the cross section for helium ionization by proton impact. (Adapted from ref. 11.)

deeper, more transparent understanding of microscopic entities, whereas quantum mechanical formalisms tend to conceal them. That is not to be understood as a defect of the quantum approach. On the contrary, given that even expert physicists find the fundamental theory of QM difficult, if not impossible, to comprehend, classical models are a useful conceptual aid.

Classical atomic physics, one might say, is the answer to the question, What would have become of theoretical atomic physics had QM not emerged? But the opposite question is also of epistemological importance: In a world viewed solely through the lens of classical mechanics, what would have emerged as the counterpart to QM? Arguably, the role of QM would have been played by classical statistical physics. In fact, probabilistic models for the scattering processes have been devised as counterparts of the quantum mechanical calculations.[15] With the help of nonlinear dynamics, many quantum effects can be reproduced with classical theory.

It's also interesting to note that just as classical methods have made meaningful appearances during the era of QM, some concepts regarded as essentially quantum mechanical can be traced back to the classical antique.[16]

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