**Table 1** Properties of Rydberg States of the H Atom

| *Quantity* | *Expression* | *Value at n, ℓ = 30, 29* |
|---|---|---|
| Binding energy (eV) | $-13.6n^{-2}$ | $-0.0151$ |
| Average potential energy (eV) | $-27.2n^{-2}$ | $-0.0302$ |
| Average kinetic energy (eV) | $13.6n^{-2}$ | $0.0151$ |
| Average orbital radius ($a_0$) | $\frac{1}{2}[3n^2 - \ell(\ell+1)]$ | 915 |

Rydberg atom, laboratory fields of strength comparable to or greater than the atomic field may be easily achieved, which allows the study of nonlinear effects in the strong perturbation regime. An interesting property of the Rydberg atom is its semiclassical character owing to the correspondence principle as $n \to \infty$. This facilitates fundamental studies such as quantum behavior of classically chaotic systems, as well as semiclassical aspects of double Rydberg atoms where two electrons are in high Rydberg states.

*See also:* ATOM; BOHR'S ATOMIC THEORY; ELECTRON; EXCITED STATE; IONIZATION; QUANTUM NUMBER; RYDBERG CONSTANT; SPECTRAL SERIES; STARK EFFECT; ZEEMAN EFFECT

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JIANYI WANG

# ATOMIC BOMB

*See* FISSION BOMB

# ATOMIC CLOCK

Atomic clocks use natural resonances within atoms (or molecules) to keep time. These "quantum mechanical oscillators" are vastly less sensitive to environmental effects, such as temperature, pressure, humidity, vibration, acceleration, and so on, than are macroscopic oscillators such as pendulums and quartz crystals. The result is that atomic clocks are the most stable and accurate clocks known.

## History

Clocks are instruments to measure the passage of time. In the period from the earliest human awareness of time until 1955, the measure of time and, subsequently, even its legal definition were based on the rotation of the earth. Clocks were first developed to help interpolate this motion and to maintain a record during intervals of darkness. During the "age of exploration" the problem of navigating during long sea voyages led to a great need for better clocks (Fig. 1). In 1759, after 35 years of work, Richard Harrison developed a "chronometer," which could keep time to ±0.4 s per day even in the harsh environment of a ship at sea. Subsequent developments to laboratory pendulum devices culminated in 1921 in the Shortt "free" pendulum in which the master pendulum was separated from the escapement mechanism. It was able to keep time to within about one millisecond per day.

In the early 1920s the electronic quartz crystal oscillator was developed. It rapidly improved to the point where it was more stable than the rotating earth. This necessitated a redefinition of the second. In 1956, the definition of the second was changed to 1/31,556,925.9747 of an orbital period of Earth around the Sun. However, advances in atomic timekeeping quickly made that definition obsolete and, in 1967, the SI (*Le Système International d'Unités;* the metric system) second was defined as ". . . the duration of 9,192,631,770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the cesium-133 atom."

## Basic Operation

Atomic clocks and atomic frequency standards (a clock is just a constant frequency generator with a counter added) are based on transitions between two energy levels in an atom or molecule. The frequency $\nu$ corresponding to a transition is given by

$$h\nu = |E_1 - E_2|,$$

where $E_1$ and $E_2$ are the energies of the two levels and $h$ is Planck's constant. The "hydrogenic" atoms that form the basis of our atomic clocks can be viewed as an electron in orbit about a nucleus. Both particles have spin angular momentum and, hence, a magnetic moment. Just as two magnets attract each other when oriented one way and repel when oriented differently (an energy difference), so too do the magnetic moments of the nucleus and the electron interact. However, according to the rules of quantum mechanics, only two precisely defined orientations are allowed: spin parallel and spin antiparallel. This leads to two energy states whose energy difference is established by the magnetic coupling between the electron and the nucleus. These states are called "hyperfine" states from their first observation as very small splittings in optical spectra. Their energy difference falls in the microwave region of the electromagnetic spectrum.

The energy difference between hyperfine states is much smaller than thermal energy at room temperature. According to the rules of a Boltzmann energy distribution, atoms are nearly equally distributed in the two energy states at room temperature. If we irradiate such an ensemble of atoms with resonant radiation, some atoms in the lower energy state will absorb a photon (the basic quantum of radiant energy) and make the transition to the upper energy state. However, an equal number of atoms in the upper state will be stimulated to emit a photon and make the transition to the lower state. There is no

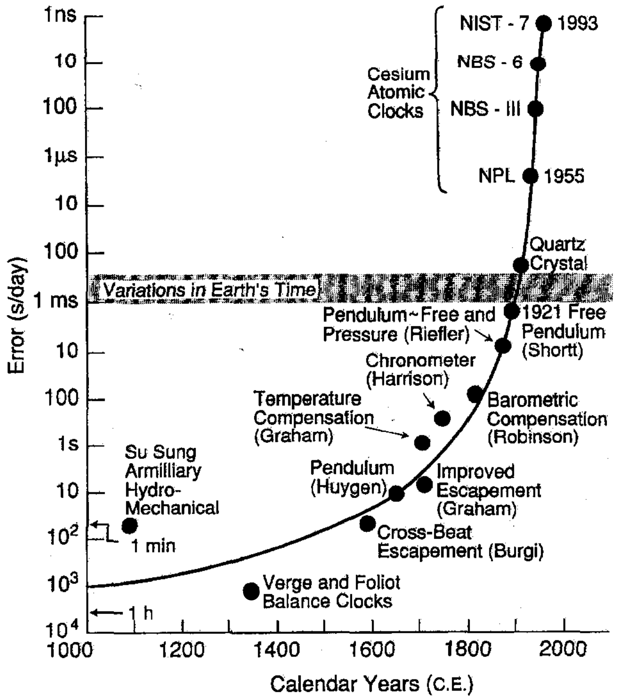


**Figure 1** Historical growth in timekeeping accuracy.

net change in either the atomic state populations or the number of photons; we have no way of knowing if the radiation was the right frequency to excite the resonance.

This, then, sets the stage for describing the operation of an atomic clock; three basic operations must happen. First, the initial population distribution must be modified. Second, the atoms must be exposed to resonant radiation to cause the transition to happen. Finally, the degree to which the atoms made the transition must be determined. Any given atom must either make the transition or not; things are quantized. However, the number of atoms that make the transition is a function of how nearly the applied radiation matches the resonant frequency of the transition. Hence the strength of the signal at the detector is a measure of the correctness of the applied frequency. In this way a "control signal" is generated and used to lock the applied frequency to the resonant frequency of the atomic transition.

Three types of atomic clocks are available commercially. We will discuss briefly the operation of each in light of the foregoing model to explain

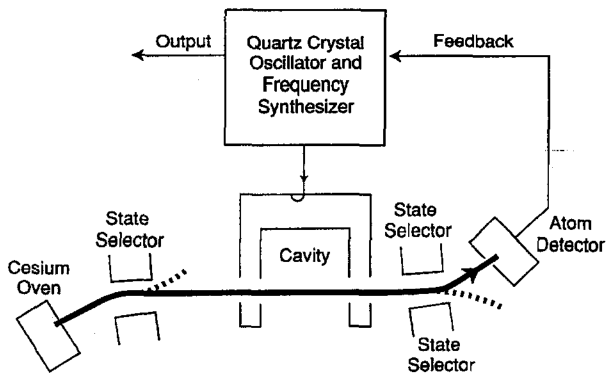


**Figure 2** Schematic of a cesium atomic beam clock.

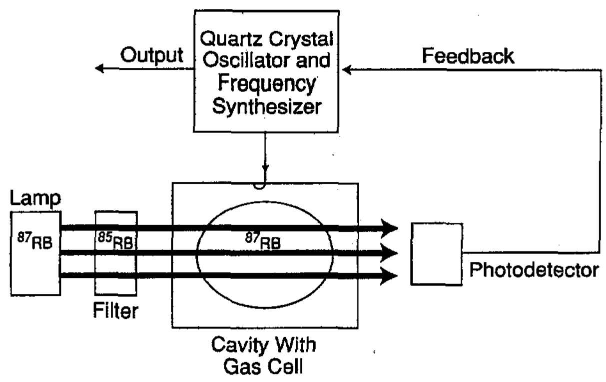


**Figure 3** Schematic of a rubidium gas cell clock.

their stability and accuracy. In this field, we call "accuracy" the degree to which a device can realize the frequency of the free and unperturbed atomic transition. "Stability" has two types: Short-term stability is dominated by random noise processes and improves with increased measurement time; long-term stability, including drift, results from changes in the perturbations to the natural atomic resonance frequency and becomes worse at longer times. Long-term stability, by this definition, must be better than accuracy.

## Examples

*Cesium beam.* The cesium clock is the first and still most accurate type of atomic clock (Fig. 2). Cesium is a gold-colored metal that melts at body temperature and has a hyperfine frequency that is set by the international definition of the second to be 9,192,631,770 Hz. The metal is contained in a small oven, where it is heated to about 100°C. While still well below its boiling point, a vapor of the atoms exists in equilibrium with the liquid. A tube leading from the oven allows some of this vapor to escape into a vacuum chamber, forming a beam of atoms traveling with thermal velocity ($\approx$ 200 m/s for cesium). The beam of atoms first passes through a strongly inhomogeneous magnetic field (a Stern–Gerlach magnet) where the trajectories are altered according to the internal magnetic state of the atom. The state-selected atomic beam then passes through a microwave cavity where it is exposed to the microwave radiation to excite the atomic transition. Finally, the atomic beam passes through a second Stern–Gerlach magnet where atoms that made the transition are directed toward a hot wire similar to the filament in a lightbulb. Cesium atoms that reach the hot filament are ionized, causing an electric current proportional to their number. The microwave frequency is controlled by this signal and is divided down to a lower frequency by electronic circuits to run a clock.

Magnetic and electric fields in cesium clocks are easily controlled, and the atoms do not touch anything during their flight. Perturbations to the "clock" transition are small and well-understood. The result is both high accuracy and long-term stability. Commercial cesium clocks are the size of a personal computer, weigh 10 to 20 kg, consume several tens of watts, and cost the equivalent of a luxury car. The annual production is several hundred units, and the lifetime of the cesium tube is 3 to 10 years. The long-term stability of the best commercial cesium clocks is of the order of 1 part in $10^{14}$, or 1 s in 3 million years. Laboratory standards have accuracy of this order.

*Rubidium cell.* Rubidium is a silvery metal that has two naturally occurring isotopes: $^{85}$Rb and $^{87}$Rb. The process of state selection and detection in this type of standard uses a technique called "optical pumping" and takes advantage of a natural coincidence in the spectroscopy of the two isotopes. The two hyperfine levels that form the clock transition exist within the lowest energy orbit of the electron, the "ground state." In the optical pumping process, atoms in one of the hyperfine states preferentially absorb light, which causes the outer electron to be excited to a higher orbit. When an electron returns to the ground state nanoseconds later, it may enter either hyperfine state. In this way, after repeated interactions with the light, all the population can be "pumped" from the absorbing hyperfine level to the other. In the rubidium cell–type standard (Fig. 3),

$^{87}Rb$ atoms are held in a glass cell and the resonant, optical-pumping light is generated by a lamp that passes an electric discharge through a vapor of $^{87}Rb$ atoms. Such a simple set-up, however, would not produce optical pumping because the lamp puts out light resonant with atoms in both hyperfine levels. The magic in the case of rubidium is that an additional cell filled with $^{85}Rb$ can be inserted between the lamp and the clock cell to filter out the light that is resonant with one hyperfine level. As the clock cell is optically pumped, the number of atoms absorbing light decreases and the amount of light transmitted through the cell increases. However, if the clock transition is excited by resonant microwaves, atoms are returned to the light-absorbing state, and the transmitted light decreases proportionally. This process is called microwave–optical double-resonance and it allows the absorption of microwave photons to be detected by their action on much more easily detected visible photons. As before, the signal from the detector is used to lock the frequency of the microwave generator to that of the atomic resonance.

This type of atomic clock can be quite small; typical units are the size of a tea cup, with advanced prototype units only 25 $cm^3$. They are relatively inexpensive and are widely used in telecommunications. The annual production is thousands of units that typically have a 5- to 10-year lifetime. Because the atoms are perturbed by both the optical pumping light and collisions with the buffer gas in the clock cell, these clocks are not as accurate or long-term stable as cesium beam devices; typical stability at a year is parts in $10^{11}$. Their short-term stability, however, is as good as the best cesium beam devices because the number of atoms in even a small cell is larger than the number of atoms passing down an atomic beam. The short-term stability is on the order of 1 part in $10^{11}$ at 1 s and improves linearly with the square root of the measurement time.

*Hydrogen masers.* This type of atomic clock (Fig. 4) differs from those just discussed in that it usually operates as an "active maser." That is, the clock transition is not probed by externally generated radiation but rather by radiation generated by the atoms themselves. It starts much like the cesium beam clock. Molecular hydrogen is contained in a bulb where an electric discharge breaks the molecular bond and creates atomic hydrogen. This is allowed to escape through a tube to make an atomic beam, which is directed through a state-selecting magnet. The magnetic state-selector is designed to focus atoms in the higher energy state into a storage bulb contained within a microwave cavity. The bulb has a specially coated wall that allows the atoms to bounce around for up to one second without destroying the carefully prepared initial atomic state. In operation, the microwave cavity is filled with photons resonant with the hyperfine transition. A state-selected atom interacting with these photons can be "stimulated" to emit a similar photon and make the transition to the lower hyperfine level. In this way, a kind of chain reaction is established where one photon stimulates the creation of another, and they in turn stimulate more. The rate at which new atoms are supplied to the cavity is adjusted to balance the loss of photons in the cavity walls. A very small amount of the microwave power (picowatts) is coupled out of the cavity and used to steer the frequency of a more powerful oscillator that runs the clock output.

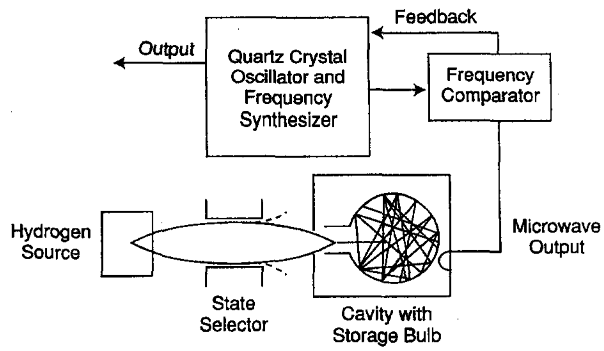


**Figure 4** Schematic of a hydrogen maser clock.

The advantage of this type of clock is its exceptional short-term stability; parts in $10^{15}$ for hours to days. Hydrogen masers are extensively used in a type of astronomy called "very-long-baseline interferometry," where the exact time is less important than very high stability over hours and days. However, the hyperfine transition frequency at 1.4 GHz is 43 times more sensitive to magnetic fields than is that of cesium. Furthermore, an aspect of the active maser action is that the atomic resonance is much more strongly coupled to the microwave cavity resonance (coupled harmonic oscillators) and is more seriously perturbed by it. We call this effect cavity pulling. These effects make the technology very difficult, requiring state-of-the-art temperature and magnetic field control. As a result, hydrogen masers are the size of a small desk and cost more than a typical house. Only a few are made each year. The cavity pulling and collisions of the atoms with the walls cause frequency biases that degrade the accuracy and lead to long-term frequency drift.

### Future Devices

Research into laser-cooled atoms and ions is pointing the way to future atomic clocks in which the perturbations to the atomic transition can be controlled to parts in $10^{18}$. It follows that the stability will be correspondingly better than the standards of today.

*See also:* Atomic Physics; Boltzmann Distribution; Energy Levels; Maser; Oscillation; Oscillator; Pendulum; Photon; Quantum Mechanics; Resonance; Stern–Gerlach Experiment

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Robert Drullinger

## ATOMIC MASS UNIT

The unified atomic mass unit (u) is defined as one-twelfth the mass of an atom of the carbon isotope $^{12}_{6}C$, that is, an atom comprising six electrons and protons and six neutrons. Measurements give its value as $1.66054 \times 10^{-27}$ kg. An Avogadro number (1 mole, about $6.022137 \times 10^{23}$) of $^{12}_{6}C$ atoms has a mass of exactly 12 g. In energy units, 1 u = 931.494 MeV/$c^2$, where $c$ = 299 792 458 m/s is the speed of light.

The International Union of Pure and Applied Chemistry adopted the current carbon standard for the atomic mass unit in 1961. This action resolved a conflict between two slightly different definitions of the atomic mass unit, both based on oxygen. Physicists employed the oxygen isotope $^{16}_{8}O$ as the standard and defined each atom of this isotope to have a mass of 16 u. Chemists, on the other hand, defined the natural isotopic mixture of oxygen to have an average mass of exactly 16 u, which some called 16 avograms. Because about 99.76 percent of oxygen on Earth are atoms of the isotope $^{16}_{8}O$, the chemical and physical scales were for most purposes essentially equal: The average isotopic mixture of oxygen has a mass of 16.00445 u on the $^{16}_{8}O$ physical scale, and the ratio of the atomic masses of the isotopic mixture of oxygen to that of the pure isotope $^{16}_{8}O$ is the Mecke–Childs factor, 1.000275. On the current $^{12}_{6}C$-based scale, the mass of an atom of $^{16}_{8}O$ is 15.99491 u and the average mass of a natural isotopic mixture of O is 15.9994 u.

The history of the atomic mass unit goes back to the beginning of the nineteenth century, when chemists were making tables of definite proportions for the formation of compounds from the elements. The English physician William Prout noted in 1815 that the weights of most atoms could be taken as multiples of the weight of the hydrogen atom. He went so far as to suggest (erroneously) that all matter consisted of hydrogen in varying amounts. A full understanding of the atomic mass unit and its application had to wait almost a century for J. J. Thomson's demonstration by means of ion-beam analysis in 1913 that some elements exist in different isotopes.

Chemists can determine average relative atomic masses by weighing the relative amounts of chemical elements needed to form compounds of known compositions, and where there are ambiguities in chemical compositions, these can often be resolved by comparing volumes of vaporized constituents or by measuring the heat capacities of gases and solids. However, since the early work of Thomson and the subsequent measurements of A. J. Dempster and F. W. Aston with mass spectrometers in 1918 and 1919, scientists have been able to determine absolute atomic masses of individual isotopes from the deflection of beams of charged ions of these isotopes in electromagnetic fields. The deflection depends both on the initial velocity and on the ratio of the charge to the mass. The velocity dependence can be eliminated since it is different for electric and magnetic fields, and the charge is found independently, for example, by balancing the force in an electrostatic field against an oppositely directed gravita-