Superconductivity and the Quantization of Energy

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Ideas about quantized energy levels originated in atomic physics, but research in superconductivity has led to unparalleled precision in the measurement of energy levels. A comparison of levels produced by two Josephson junctions shows that they differ by no more than 3 parts in 10^{19} at an energy of 0.0003 electron volt. The fact that the myriad of interactions of 10^{12} particles in a macroscopic body, a Josephson junction, can produce sharply defined energy levels suggests a dynamical state effectively divorced from the complexities of its environment. The existence of this state, the macroscopic quantum state of superconductors, is well established, but its isolation from intrinsic perturbations has recently been shown to be extraordinary. These new results, with an improved precision of about ten orders of magnitude, are discussed in the context of highly accurate results from quantum electrodynamics, atomic spectroscopy, and the standards of metrology. Further refinements in precision may be achievable at higher energy levels, about 12 electron volts, as they become available from a new series array of 18,992 Josephson junctions.

Microscopic things can be identical, macroscopic things cannot. This proposition is so imbued in the minds of physicists that it is interesting to see that it is false in the following sense. In the past physicists believed that only atoms and molecules could have identical states of energy, but recent experiments have shown that much larger bodies, superconductors in macroscopic quantum states, have equally well-defined energies. Moreover, these states provide tests of theory that are as delicate as tests of quantum electrodynamics based on electrons, for example. To describe the origin of the proposition and its negation, I begin with a synopsis of some of the more accurate measurements in science.

Finely engraved lines on a metal bar were used for many years to define the international standard for length measurements, the meter. This standard was inferior to its successor, which was based on the wavelength of the orange-red emission line of ^{86}Kr. This new standard gave higher accuracy, a few parts in 10^9, primarily because it was based on an intrinsic property of an atom: the wavelength of emission from a narrow spectral line (*1, 2*). Similarly, the best clocks are atomic clocks: the hydrogen maser, with a stability of about 1 part in 10^{15}, for the measurement of intervals of an hour or so, and an atomic beam machine based on ^{133}Cs, with an uncertainty of about 2 parts in 10^{14}, for the measurement of intervals of a day and longer (*3*). These standards were designed to make performance depend primarily on the properties of individual isolated atoms. In this scheme it is of central importance that atoms of the same species have identical properties. This contrasts with the properties of a solid body, for example, a quartz crystal oscillator, wherein the properties of the quartz are different from one body to the next. All efforts to make identical quartz plates will be frustrated by slightly different impurities, different crystalline imperfections, and slightly different overall geometry. Thus, microscopic things can be identical, macroscopic things cannot.

The essence of science is the comparison of conceptual models, in this case mathematical models, with experimental results. The prime example of agreement between theory and experiment for atomic physics comes from the simplest of atoms, H. As an example of the status of this theory, consider calculations of the hyperfine interval of the ground state, the energy levels that are the basis for the hydrogen maser. This quantity is $\nu_{\text{theory}} = 1420.403 \pm 0.001$ MHz. The main contribution to this calculation comes from electromagnetic interactions as described by quantum electrodynamics (QED), but the strong nuclear force contributes 34 parts in 10^6. Inaccuracy in the evaluation of the latter contribution produces the stated uncertainty in ν_{theory}, about 0.7 parts in 10^6. Measurements of this frequency have been made with far greater accuracy than the foregoing theoretical prediction. The present experimental value for the hyperfine splitting is $\nu_{\text{expt}} = 1420.405\ 751\ 767 \pm 0.000\ 000\ 001$ MHz. This is an uncertainty of 0.7 parts in 10^{12}, which is about six orders of magnitude smaller than that obtained from theory (*4*).

A more stringent comparison of theory and experiment can be obtained from measurements on systems without nuclei. Consequently our attention is drawn to experiments with electrons and photons only. The experimental value for the magnetic moment of the electron (*5*), in units of the Bohr magneton, is 1.001 159 652 188 ± 0.000 000 000 004. The theoretical value of this quantity (*6, 7*) has an uncertainty seven times as large as the experimental value, but it is in agreement with experiment. Thus there is agreement at approximately 3 parts in 10^{11}, which implies that this theory is more accurate by about four orders of magnitude than the theory of the H atom, at least insofar as the latter has been evaluated.

These results give a quantitative feel for what is meant by high accuracy in experimental and theoretical atomic physics. They also illustrate why physicists came to the view that the best high-accuracy experiments and the best tests of physical theory were expected in this realm. That picture has changed as solid-state physics has provided remarkably accurate results. The first step was the work of Taylor, Parker, and Langenberg (*8*), who showed that the Joseph-

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son effect (*9*) provides an accurate value of the fine structure constant divided by the electronic charge. The next major step was the discovery of the quantum Hall effect by von Klitzing, Dorda, and Pepper (*10*); it gives an accurate measure of h/e^2 (where h is Planck's constant and e is the charge of the electron) and, thereby, a value for the fine structure constant $\mu_0 ce^2/2h$, where μ_0 is the permeability of free space, and c is the speed of light. The most recent development is the experimental revelation (*11–13*) that the energy levels provided by the Josephson effect are extraordinarily sharp; they have been shown to be reproducible with an uncertainty of no more than 3 parts in 10^{19}. This result is particularly striking because Josephson junctions consist of about 10^{12} atoms, a comparably large number of degrees of freedom, and unknown impurities and imperfections. It was not expected that anything so complex could produce something as pure and sublime as the sharpest set of energy levels now known to physics. It violates the popular view that precision is intimately related to simplicity. What produces this seemingly magical result is coherence, quantum mechanical coherence of the macroscopic object.

The macroscopic state has other implications, notably discussed by Leggett (*14*) in relation to Schrödinger's cat paradox. A review of that subject from an experimental point of view, but ignoring the cat, has been provided by Clarke *et al.* (*15*). The energy levels discussed in that reference should not be confused with those of the present discussion; they are physically distinct.

Superconductors and the Macroscopic Quantum State

The originator of the macroscopic wave function was London (*16*), who conjectured that superconductivity is the result of a condensation in momentum space. A sufficiently narrow range of momentum for the electric charge carriers implies, through the uncertainty principle, that their wave function is coherent over distances much greater than the sizes of atoms. Combining this idea with the requirement that the wave function be single-valued at each point inside the superconductor, London drew the novel conclusion that a closed ring of superconductor, with a circulating current around the ring, could have only quantized values of magnetic flux through the ring. Experimental confirmation of these ideas was provided by Deaver and Fairbank (*17*) and by Doll and Nabauer (*18*) in 1961. The value of the flux quantum is $h/2e$.

Mathematical models of physical systems are usually constructed as simply as possible for the desired accuracy of description. For example, the theory of the H atom must include the Coulomb interaction between the proton and the orbital electron as well as the effects of the spins and magnetic moments of these particles, but it is adequate for many purposes to ignore the strong forces within the nucleus (proton), which is equivalent to assuming that the proton has zero radius. The motivation for using a macroscopic wave function for superconductors comes, in part, from asking, What is the simplest mathematical form for capturing essential features of superconductivity (*19*), such as flux quantization and the Josephson effect? Not all the physics of the system will be included in this description. For example, the fundamental theory of superconductivity, developed by Bardeen, Cooper, and Schrieffer (BCS) (*20*), describes the zero temperature state of superconductors in terms of conduction electrons that are paired. Each pair is held together by an attractive force. At temperatures above absolute zero some of the pairing bonds are broken. The resulting unpaired electrons, or quasi-particles, play a role in our later discussion. The macroscopic wave function describes the physics of electrons in pair states only. We write this wave function as

$$\Psi(r,t) = \Psi_0 e^{-i\theta(r,t)} \tag{1}$$

where the interesting physics will come from the phase $\theta(r,t)$, where r is a space coordinate and t is time. Using a single phase variable for the superconducting state is equivalent to saying that the state is coherent. We view this wave function as describing a large number of pairs, all doing the same thing. Instead of using the energy of the total number of particles for the Hamiltonian, we can use a one-particle description, for which we know the energy is the electrochemical potential μ.

Josephson junctions are typically made by depositing, on top of an insulating substrate, a thin film of superconductor, whose upper surface is then coated with a very thin insulating layer, about 1 nm thick. The junction is completed by depositing an additional thin film of superconductor on top of this layered structure. This process produces a device with typical dimensions 10 by 10 by 0.4 μm. The insulating barrier between the superconducting layers is thin enough to allow weak coupling between the superconductors by electron tunneling. For this system the Schrödinger equation is

$$i\hbar d\Psi_1/dt = \mu_1\Psi_1 + T\Psi_2 \tag{2}$$

where the subscripts 1 and 2 refer to the superconductors on the bottom and top of the junction, respectively. This equation, along with its twin in which subscripts 1 and 2 are interchanged, describes how the superconductors on the two sides of the junction influence each other through the tunneling characterized by the coefficient T. The difference in electrochemical potentials across the junction, for an applied voltage V, is

$$\mu_1 - \mu_2 = 2eV \tag{3}$$

The electric charge $2e$ appears in this equation because the electrons are paired. Together these equations give a general description of the problem of interest.

Setting $V = 0$ and solving the equations, we obtain the Josephson equation relating the phase difference, $\theta_1 - \theta_2$, across the tunneling barrier, to the current through the barrier or junction

$$I = I_0 \sin(\theta_1 - \theta_2) \tag{4}$$

The quantity I_0, the critical current of the Josephson junction, is proportional to the tunneling coefficient T of Eq. 2.

The solution of Eqs. 2 and 3 with arbitrary voltage V is the same as that of Eq. 4 but with the added feature that the time rate of change of the phase difference, defined as the frequency ν, is proportional to V,

$$\nu = K_J\ V \tag{5}$$

where the important constant K_J is given by

$$K_J = 2e/h \tag{6}$$

in conventional theory. Thus if a steady voltage is applied, then the current in the junction oscillates at a frequency that is approximately 484 MHz/μV. Equations 4 through 6 are the Josephson equations.

With these equations we can consider the effects of more complex bias conditions such as both a steady and an alternating voltage, at frequency ν_1, applied to the junction. For this case a striking phenomenon occurs: there are ranges of steady current (dc) over which the average voltage across the device remains constant. These characteristic or eigenvoltages are

$$V_n = n\nu_1/K_J \tag{7}$$

where n can have positive and negative integer values. The first eigenvoltage V_1 occurs for ν of Eq. 5 equal to ν_1, V_2 for $\nu = 2\nu_1$, and so on. Experimentally the applied frequency ν_1 has been raised as high as the far-infrared to make the voltage V_n as large as possible

(21), but a better strategy for high voltage is to use a lower frequency, about 90 GHz, and to raise the effective n by cascading many junctions.

If we multiply the eigenvoltage by the charge $2e$, we find the energy eigenvalues

$$E_n = nh\nu_1 \tag{8}$$

These eigenvalues are the same as those of that classical problem of physics, the harmonic oscillator.

Atomic energy levels are notably different from these. Spectral emissions from gas in an electrical discharge can be analyzed to determine the atomic species of the gas because the energy levels that are the origin of the spectra are unique to an atomic species. The quantized energy levels from superconductors have just the opposite property: their energies are independent of the material producing them. Experiments with the new metal oxide superconductors confirm this conclusion for those materials as well (22).

I have used the macroscopic wave function to derive the Josephson relations, but these relations have deeper roots, as I will discuss later. The main point of interest here is that Eqs. 5 through 8 may be among the most accurate equations in physics. The question has been repeatedly asked whether K_J is exactly $2e/h$ or whether that is an approximation. No corrections or errors have been found with the use of the most sensitive experimental tests, as I will now discuss.

Experimental Results

How accurately can these energy eigenvalues be experimentally measured or compared? Because the energy is directly proportional to the frequency ν_1 of the radiation applied to the Josephson junction, we see immediately that the eigenstates cannot be defined better than the frequency ν_1. This experimental problem can be eliminated if one uses two Josephson junctions, both of which are irradiated by the same oscillator, so that small variations in applied frequency will have the same effect on both junctions. Thus the physical question becomes: With each junction producing its own voltage V_n from a common applied frequency ν_1, how nearly equal will the voltages be? This is equivalent to asking whether K_J is the same for both junctions. Can macroscopic objects produce identical voltages?

The experiment of Tsai, Jain, and Lukens (11), which is a refinement of an experiment by Clarke (23), is shown schematically in Fig. 1. It is an experiment to compare the voltages of two sources in a superconducting loop. Each source is in fact a Josephson junction biased at voltage V_n. A difference in voltage between the sources ΔV produces a current I in the circuit according to the relation

$$I = (1/L)\int \Delta V \, dt \tag{9}$$

where L is the inductance of the circuit. This experiment is very sensitive to differences in voltage because L can be rather small and we can wait for hours, if necessary, to detect a change in the current.

Several different types of Josephson junctions have been used in this type of experiment. Let us first consider the experiment of Tsai *et al.* (11), in which one of the Josephson junctions was an In microbridge and the other was a Nb-Cu-Nb junction. The point of this experiment was to see whether different voltages would be produced when Josephson junctions made of different materials were irradiated with the same frequency. This experiment was performed with radiation at 18 GHz and with both junctions biased on their first voltage step (n = 1), for which the voltage was 36 μV. Over a 5-hour period, the loop current had small random variations with no significant linear component. This implied an average voltage difference between the junctions of less than 2×10^{-21} V. Thus K_J is the same for these two junctions within 6 parts in 10^{17}.

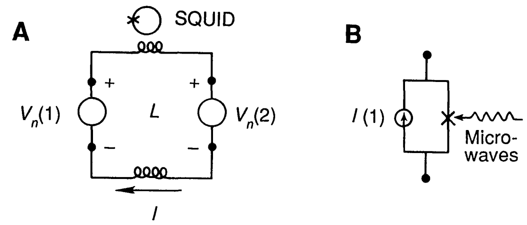

Fig. 1. (**A**) Superconducting circuit for detecting differences in the voltages $V_n(1)$ and $V_n(2)$. The SQUID (superconducting quantum interference device) is an amplifier that provides a sensitive means for detecting changes in the current I. (**B**) Each voltage source of (A) is in reality a Josephson junction, denoted here as X, that is biased by dc and microwaves.

In an experiment by Jain, Lukens, and Tsai (12) tunnel junctions made of Pb alloys were used for both junctions. In this case, larger junction voltages were available and other refinements had been made in the apparatus. Using ninth-order voltage steps at approximately 300 μV and an observation time of 10 hours, they found that the average voltage difference between the junctions, with 2σ error limits, was $(3 \pm 6) \times 10^{-23}$ V. The interpretation of this experiment was more complicated than that of the first one because its increased precision brought it into the sensitivity range for corrections from general relativity. However, these corrections, at the level of 10^{-21} V, were shown to have a null effect overall. Consequently, we conclude that the K_J values for the two junctions differ by no more than 3 parts in 10^{19}, the maximum 2σ deviation from zero voltage.

The final experiment to be discussed is much the same as those above; the main difference is the replacement of the individual Josephson junctions by a series array of junctions. Arrays were developed to provide voltages that are larger than those available from single junctions. The voltages compared in this experiment are at the 1-V level rather than the submillivolt level. This is the work of Kautz and Lloyd (13), which is complementary to that of Niemeyer *et al.* (24). In this experiment two arrays, each with 2076 tunnel junctions, made of Nb-NbO_x-Pb alloy, were used with applied radiation at 90.5 GHz. The effective step number n for this experiment was 5423, which implies a voltage of 1.015 V. The quantized voltages from a similar array are illustrated in Fig. 2. Occasionally one of the junctions in an array will lose phase lock because of a noise transient. Consequently, the measuring times are less than in the single-junction experiments. With a 0.43-hour observation time, the average voltages of the two arrays differed by less than 2 parts in 10^{17}. This is less precise than the best result with a pair of single junctions, discussed above, but it is consistent with that result. Moreover, it comes from different apparatus, with quite different superconducting circuits, and it was obtained by different experimentalists.

The belief persists that the larger voltages available from arrays will provide a means for improving the precision of these voltage comparison experiments. If that is so, then the newly developed array with 18,992 Josephson junctions (25), which produces quantized voltages up to 12 V, will offer an inviting opportunity when it is sufficiently refined.

Discussion of Results

The precision (26) of 3 parts in 10^{19} achieved in the experiment discussed above (12) is greater by approximately ten orders of magnitude than that of the prior work on the comparison of quantized voltage levels (23, 27, 28). At this new level of precision it is interesting to compare the results from superconductivity with those from a somewhat analogous experiment in atomic physics: a comparison of the frequencies of two lasers locked to the same resonance. The analogy is crude because the laser experiment depends on a servo control system and the superconductor experiment does not. Nevertheless, the precision achieved with the lasers is about 1 part in 10^{16} (29).

The comparison of voltages from the In microbridge and the Nb-Cu-Nb junction shows that K_J is not dependent on the details of construction of the junctions, even when different superconductors are used and different mechanisms are provided for weakly coupling one superconductor to the other. Performance of these devices as frequency-to-voltage converters is independent of the materials used in the junctions to a precision of 6 parts in 10^{17}.

When the junctions used in the comparison experiment are tunnel junctions, each with the same nominal composition and geometry, K_J is the same to a precision of 3 parts in 10^{19}. Remember that these junctions are macroscopic objects; they are not identical, although they are nominally the same. They differ somewhat in geometry, chemical impurities, critical current, electrical capacitance, and temperature, but their frequency-to-voltage relations do not differ.

Is it justified to conclude that the constant relating voltage to frequency is $2e/h$? The answer is yes at an accuracy (26) of a few parts per million because the voltage and frequency, as well as $2e/h$, have been independently determined to that accuracy. The intriguing scientific question is whether K_J equals $2e/h$ for accuracies much greater than those for which the value of $2e/h$ is presently known. An answer to this question can be obtained only by a combination of theory and experiment. Kinoshita (30) noted there are at least three levels at which this question can be addressed by theory: level 0, fully relativistic quantum theory; level 1, a Hamiltonian with electrons and nuclei interacting nonrelativistically; and level 2, the effective mass approximation and quasi-particle description, the usual domain of solid-state theory. Use of the macroscopic wave function, as above, should be regarded as a level 3 theory.

A level 0 theory by Nordtvedt (31), pertaining to a QED renormalization of the electron's charge inside a metal, yields a material-dependent correction to K_J of the order of 10^{-10}. The experiment of Tsai *et al.* (11), with junctions composed of different materials, shows equality of the K_J values to a precision of 6 parts in 10^{17}, a contradiction with the theoretical analysis. Before the definitive experiment was done, Langenberg and Schrieffer (32), as well as Hartle, Scalapino, and Sugar (33), argued from several perspectives that Nordtvedt's conclusion was incorrect and furthermore that there are no level 0 corrections to the relation $K_J = 2e/h$.

Bloch's analysis (34) is often cited as proving the exactness of the frequency-voltage relation. Kinoshita (30) noted that Bloch's work is an attempt to connect level 2 to level 1 or level 0. Bloch's analysis is based largely on the most fundamental principles: invariance under gauge transformation and under time reversal, along with the requirement of a single-valued wave function and the assumption that all relevant charges are integral multiples of e. He makes no assumptions about the nature of microscopic interactions in the superconductor, such as the pairing mechanism of BCS theory (20). [Anderson (35) and Fulton (36) also have argued for the exactness of the relation $K_J = 2e/h$. Stephen (37) and Scully and Lee (38) have considered a correction to this relation, but their arguments have been countered by McCumber (39).]

Although Bloch's argument regarding the absence of corrections is compelling, it is not totally persuasive because he makes the assumption that the system is reversible, which leaves open the possibility of corrections arising from irreversible processes, either dissipative or other nonequilibrium effects. Dissipation occurs for the dc and microwave currents in the tunneling barrier and in superconductors with microwave current.

A widely used circuit description for a Josephson junction is the resistively shunted junction model (40) in which a resistor shunts an ideal (lossless) Josephson junction. This model can be used to explore two effects: the effect of a shunting current on a quantized voltage level and the effect of the Johnson noise of a resistor on the levels.

Several conclusions regarding the effect of resistance on the circuit can be drawn from a study of this model. The analysis takes two forms: numerical solutions of nonlinear differential equations (41) and approximate algebraic solutions valid for small applied microwave currents (42). A summary of the results is as follows. The time-averaged curves of current (dc) versus voltage exhibit ranges of current over which the voltage remains constant. These are the quantized voltage levels we have designated as V_n. The nth-order voltage step corresponds numerically to the range of dc over which the junction current makes exactly n oscillations during one cycle of the applied microwave current. We refer to this process as phase locking between the Josephson oscillations, described by Eq. 5, and the applied microwave current. Thus the range of current over which the voltage remains on a particular quantized level is equal to the range of current over which the junction can maintain phase lock. Remember that the quantized voltage levels were found earlier from the macroscopic wave function, which does not include a mechanism for dissipation. Now we see that they survive when dissipation is included.

When the usual model for Johnson noise is included with the resistor in the circuit model, we find that the voltage steps have rounded corners, which means that the average voltage changes slowly and continuously from the quantized value as the end of the step is approached. Thus, at a particular value of current, it is ambiguous whether the junction voltage is or is not quantized: an unsatisfactory state of affairs. One can eliminate this problem by using a design for which there are no stable points in the current-voltage curve except the quantized levels (43). I will not discuss this subject in detail, but the experimental results are illustrated in Fig. 2. The inclusion of dissipation and noise from a shunt resistance does not lead to errors in this case.

A condition that can lead to errors is nonequilibrium between electrons in pair states and those in quasi-particle states, as occurs very near a junction. Theory says that a normal-metal lead-wire connected to a superconductor senses the quasi-particle electrochemical potential, not the potential of the pairs. The Josephson relations are based on the pair potential, so a deviation from Eq. 7 would occur if the potentials differ. However, experiment and theory (44) show that this effect is negligible if the normal electrodes are at a distance on the scale of a millimeter from the Josephson junction. A closely related effect from thermal gradients (44) must also be taken into account.

Fundamental Significance

I want to emphasize the novelty of the Josephson effect in revealing the precision of nature in a macroscopic object. Two Josephson junctions, in spite of their complexity and dissimilarities, produce quantized energies that are identical so far as can be determined experimentally. Atomic physics has no stronger claim to identical energy levels. A precision of 3 parts in 10^{19} from solid-state physics evokes a sense of wonder, a sense of the mysterious akin to Einstein's remark (44a): "The most beautiful experience we can have is the mysterious. It is the fundamental emotion that stands at the cradle of true art and true science."

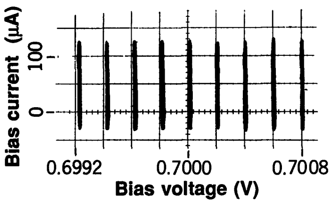

Fig. 2. Oscilloscope trace of the quantized voltage levels from a 2076-junction array driven at 96 GHz. The levels are separated by 198 μV; the current range of each step is about 155 μA (data courtesy of C. A. Hamilton).

What is responsible for this ideal behavior? I have briefly described the mechanics of the formation of the quantized voltage levels. The central point is the phase locking of the applied frequency ν_1 with the oscillations of the macroscopic wave function at frequency ν, given by Eq. 5. An energy barrier (*45*) prevents the breaking of phase lock by perturbing forces such as the electrical noise associated with energy dissipation. Other nonequilibrium processes occur in the immediate vicinity of a junction, but these processes have a null effect on the dc voltage measured at sufficient distance from the junction. What is surprising is that no interactions among the 10^{12} particles in the junction interfere with this simple process.

It is especially interesting that in other realms of physics, at some level of accuracy, the theory becomes incalculable. For the H atom, the limitation was the uncertainty of strong force effects at an accuracy of 1 part in 10^6. In a "pure" QED system, such as the electron in a magnetic field, theory is much more accurate, but effects from strong and weak forces contribute at an accuracy of 10^{-12} to 10^{-14} (*30*). For superconductors no such corrections have been seriously suggested.

"Give me a frequency and I will give you a quantized voltage. The voltage will be as well defined as the frequency." This statement summarizes the practical qualities of the Josephson effect as a frequency-to-voltage converter. The input frequency can be specified to 2 parts in 10^{14}, the accuracy of the primary frequency standard. In view of the experiments discussed here, I believe the voltage from a Josephson junction can be reproduced at approximately the same level of precision as the frequency. To assign a numerical value in volts we must have a value for K_J, a quantity that is independently known with an accuracy of only a few parts per million. This implies that the output voltage of the junction can be reproduced with a precision about nine orders of magnitude greater than it can be specified in conventional units. To circumvent this problem, K_J has been given a defined value that is consistent with the best known value of $2e/h$, namely, 483.5979 MHz/μV (*46*).

The voltage comparison experiments go well beyond the precision of 2 parts in 10^{14}, however. What is the significance of that? A summary will help clarify the situation. All of the technical difficulties that can cause errors in the observation of the quantized energy levels from the Josephson effect can be avoided without undue difficulty, so far as is known at the present time. Experiments designed to find possible variations of K_J among different Josephson junctions universally yield null results, with precisions in the range of parts in 10^{17} to parts in 10^{19}. Furthermore, the entire body of theory provides no credible basis for believing that K_J is anything other than $2e/h$. It is impossible for experimental science to confirm the validity of an equation in an exact sense. To put this in perspective, let me note that the hallowed law of the conservation of energy is empirically known to be valid with no greater accuracy than 1 part in 10^{15} (*47*). Consequently, it is fitting to believe that the Josephson frequency-voltage relation, with $K_J = 2e/h$, is among the most accurate relations in physics.

We arrived at Eq. 8 through the macroscopic wave function. Another view is that, apart from the integer n, this equation is the definition of Planck's constant, in which case Eqs. 6 and 7 are a relation between energy at frequency ν_1 and energy at zero frequency $2eV_n$—which is to say that these equations are just a statement of the conservation of energy. It is surprising that dissipative processes, which are clearly present, play a negligible role at the accuracy of the present experiments. To the extent that Eqs. 6 and 7 are accurate to 3 parts in 10^{19}, we can say that energy conservation is established at that level of accuracy, which is about four orders of magnitude beyond previous experimental tests, with the Mössbauer effect (*47*).

The most accurate value of the fine structure constant, with an uncertainty of less than 1 part in 10^8, is obtained from measurements of the electron magnetic moment. One can obtain independent values of the fine structure constant by using the Josephson effect and the quantum Hall effect (*7, 48*). When these evaluations are done with sufficient accuracy, they will test the consistency of QED and solid-state theory. The most exciting prospect is that such a test might reveal a failure of QED, which would have wide ramifications for physics. The quest begun by Taylor, Parker, and Langenberg (*8*) continues.

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26. Precision is the degree of agreement among a series of measurements. It may be quantitatively expressed by the standard deviation σ or by some other measure of uncertainty. Jain *et al.* (*12*) use a 2σ uncertainty. Tsai *et al.* (*11*) and Kantz and Lloyd (*13*) do not give statistical uncertainties, only maximum observed variations. Consequently the statements of precision given here are only approximately comparable to each other. Accuracy is the degree of conformity of a measured value to its definition.
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Research Article

Imaging Surface Atomic Structure by Means of Auger Electrons

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Measurements of the complete angular distribution of Auger electrons emitted from well-defined platinum[111] single-crystal surfaces have led to the discovery that the distributions are composed of "silhouettes" of surface atoms "back lit" by emission from atoms deeper in the solid. Theoretical simulations of Auger electron angular distributions based upon atomic point emitters and spherical atomic scatterers of uniform cross section are in close agreement with these experimental results, but opposite to previous theoretical predictions. In view of the definitive results obtained and the straightforward agreement between theory and experiment, angular distribution Auger microscopy (ADAM) is useful for direct imaging of interfacial structure and investigation of electron-solid interactions in the physical and biological sciences and engineering. Applicability of ADAM is illustrated by images obtained for monolayers of silver and iodine on platinum[111].

EXCITATION OF AN ATOM, SUCH AS BY A FAST-MOVING electron or x-ray, can result in the removal of a core electron, followed by a relaxation process in which an outer electron fills the core vacancy and a third electron, an "Auger electron," is ejected from the atom. Auger electrons were first recognized by Pierre Auger in cloud chamber experiments (*1*), and were found to have discrete energies characteristic of the emitting elements. Auger electron spectroscopy has since found wide application for elemental identification and analysis (*2*). In the course of that work, Auger signals from solid samples were found to vary significantly with the direction of emission from the surface (*3, 4*). Based upon relatively limited data, these variations have been mistakenly attributed to anisotropic emission from individual atoms, to diffraction, to multiple scattering or to a combination of these effects (*5–20*). In an effort to more clearly understand the nature of Auger electron angular distributions, we designed and constructed instrumentation capable of measuring Auger emission over the full range of angles above a solid surface. The resulting observations reveal that the measured angular distribution contains the "silhouettes" of near-surface atoms "back lit" by Auger emission originating from atoms deeper in the solid.

Theoretical simulations based upon isotropic Auger electron emission from atomic point-emitters and scattering by spherical atomic scatters of uniform cross section are in close agreement with the measured angular distributions. Best agreement occurred when the radii of the scatterers were taken to be 60 to 90 percent of their atomic radii, and the scatterers were 40 percent transparent.

Other mechanisms, such as anisotropic emission, diffraction, or multiple scattering, are not needed to explain the observed results. These experimental and theoretical findings reveal the potential usefulness of such measurements, which we have termed "angular distribution Auger microscopy" (ADAM), as a tool for imaging atomic and molecular structure at interfaces, as well as a means by which to study the interaction of electrons with matter.

Measurement of Auger electron angular distributions. The experimental apparatus employed for ADAM is illustrated in Fig. 1A (*21*). The measurements were performed in an ultrahigh vacuum chamber operated at a pressure below 10^{-7} pascal (10^{-12} atm) to preserve sample cleanliness and to permit the unobstructed travel of electrons. To stimulate Auger emission, a 3-mm^2 portion of the sample was irradiated with a 4-μA electron beam at 2000-eV kinetic energy, impinging on the [111] plane at 79° from the surface normal (toward the [001] plane). (Smaller beam currents should be used with samples sensitive to beam damage.) The resulting Auger emission (65 eV) was angle-resolved (±0.7°) with the use of collimating apertures. Energy resolution was accomplished by means of an electrostatic analyzer; the electrons passing through the energy analyzer were modulated with an amplitude equivalent to ±10 eV at a frequency of 1 kHz, amplified, counted, synchronously

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