

Origins of the Theory of Superconductivity

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Theoretical remark on the superconductivity of metals*

A. Einstein

translated by Bjoern S. Schmekel (Cornell University)[†]

The theoretical oriented scientist cannot be envied, because nature, i.e. the experiment, is a relentless and not very friendly judge of his work. In the best case scenario it only says “maybe” to a theory, but never “yes” and in most cases “no”. If an experiment agrees with theory it means “perhaps” for the latter. If it does not agree it means “no”. Almost any theory will experience a “no” at one point in time - most theories very soon after they have been developed. In this paper we want to focus on the fate of theories concerning metallic conductivity and on the revolutionary influence which the discovery of superconductivity must have on our ideas of metallic conductivity.

After it had been recognized that negative electricity is caused by subatomic carriers of particular mass and charge (electrons), there were good reasons to believe that metallic conductivity rests on the motion of electrons. Furthermore, the fact that heat is conducted much better by metals than by non-metals as well as the Wiedemann-Franz law about the substance-independence of the ratio of electric and thermal conductivity of pure metals (at room temperature) led to attribute the thermal conductivity to electrons as well. Under these circumstances there were reasons for an electron-based theory of metals similar to the kinetic gas theory (Riecke, Drude, H. A. Lorentz). In this theory free electron motion is assumed which resembles gas molecules with thermal mean kinetic energy $3/2 kT$ neglecting collisions

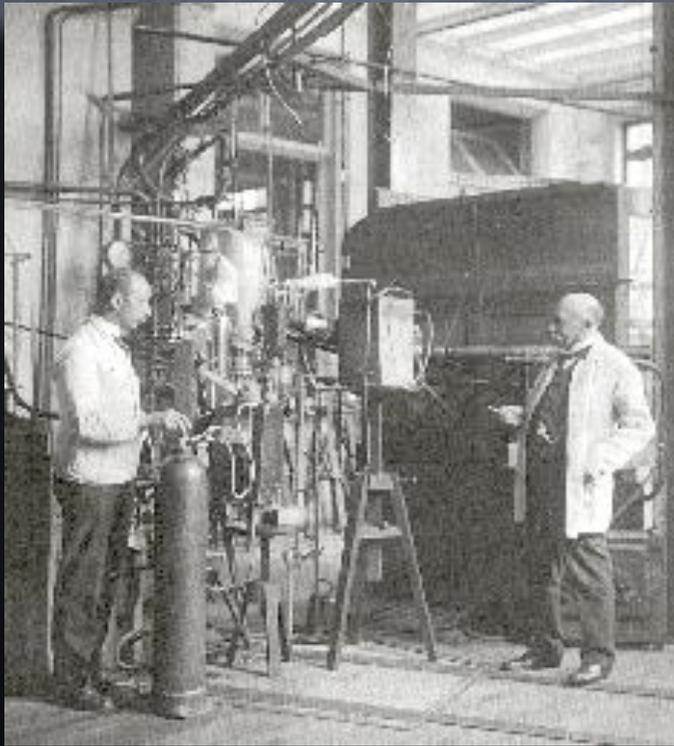
*from “Gedenkboek aangeb. aan H. Kamerlingh Onnes, eaz. Leiden, E. IJdo, 1922, pp. 435” / translated with courtesy of the Kamerlingh Onnes Laboratory, Leiden - Institute of Physics, Leiden University

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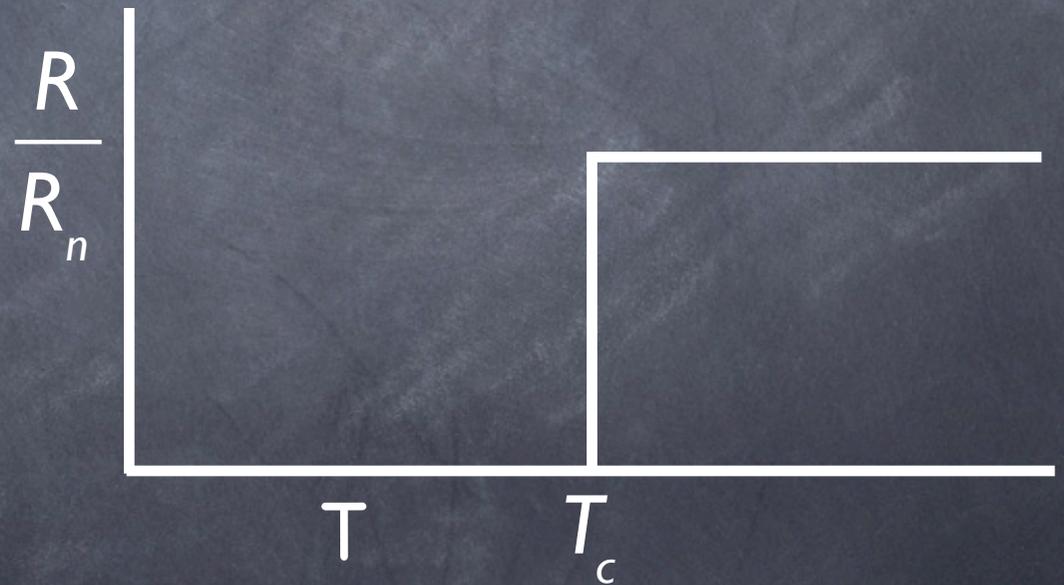
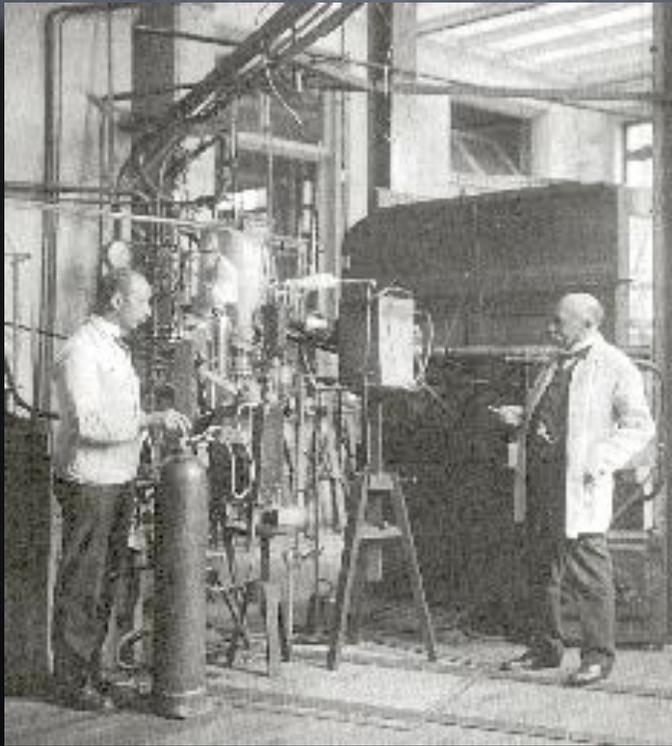
The Simple Facts of Superconductivity (as of 1955)

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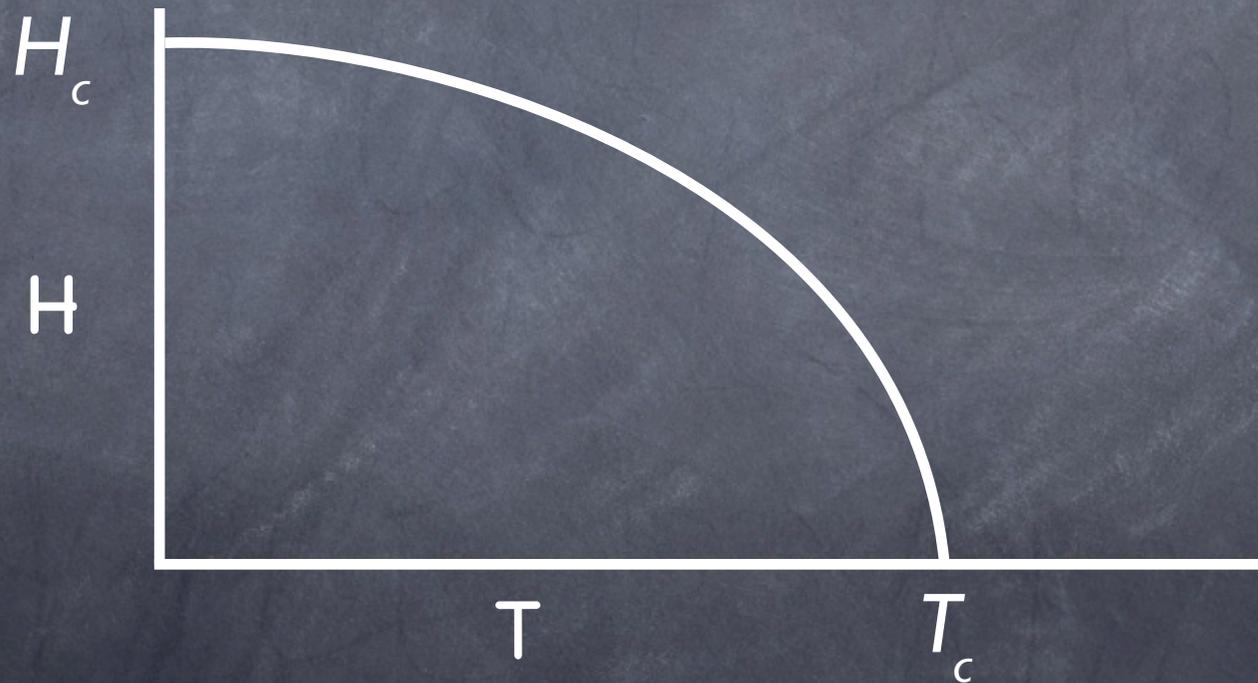


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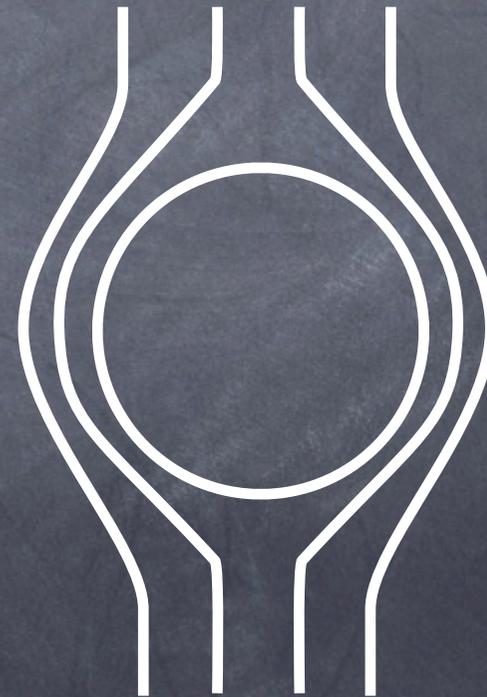


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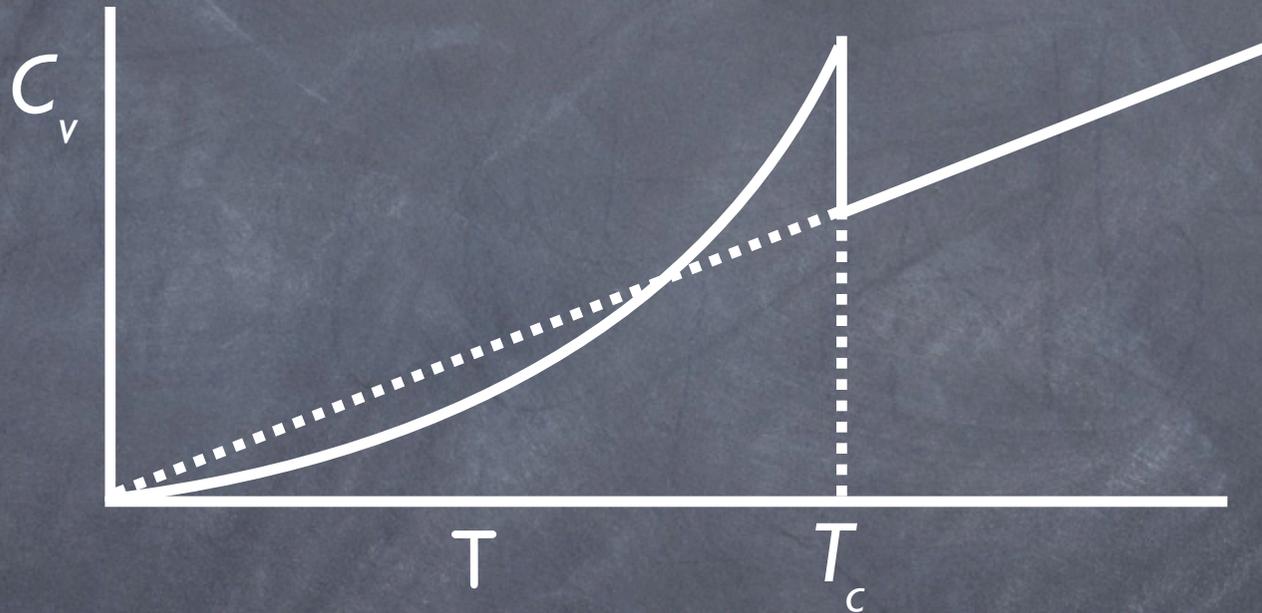
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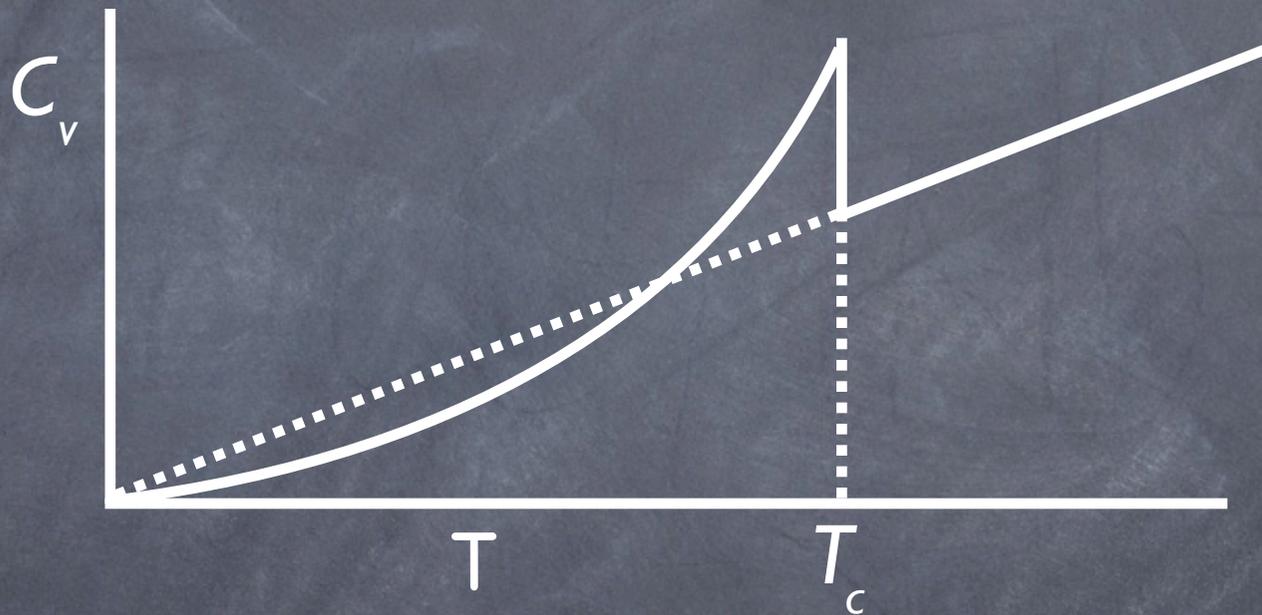
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This and other evidence, indicates the existence of an energy gap in the single particle electronic energy spectrum.

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This is known as the isotope effect and indicates that the electron-phonon interaction is implicated in the transition into the superconducting state.

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Some superconductors seem to have no energy gap and others show no isotope effect.

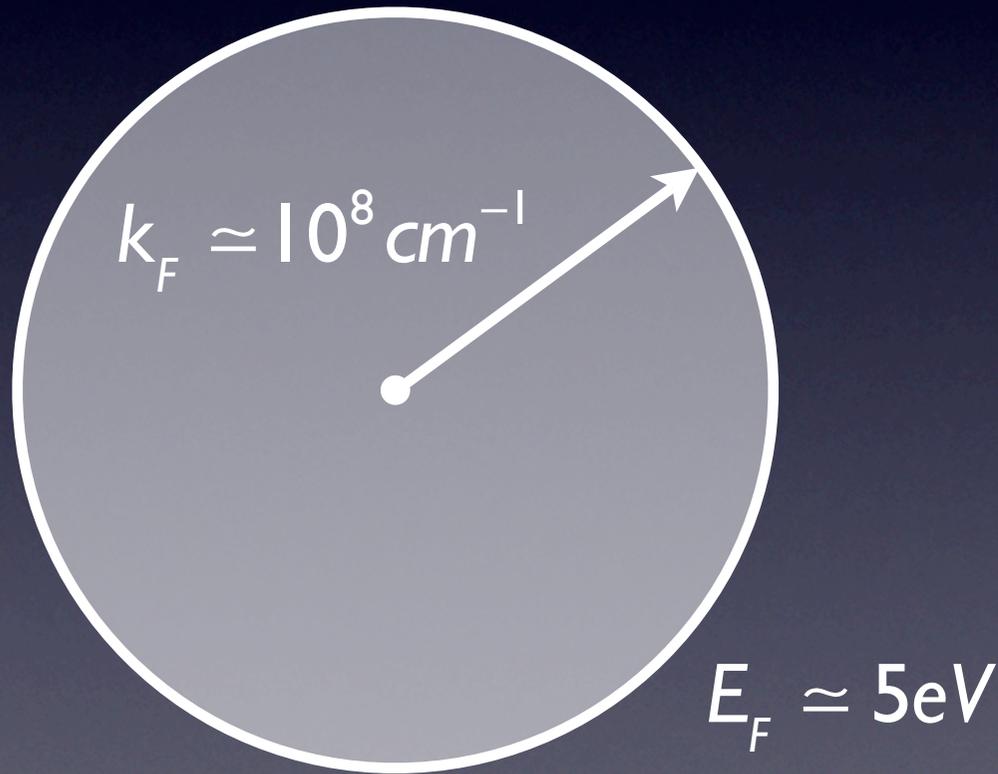
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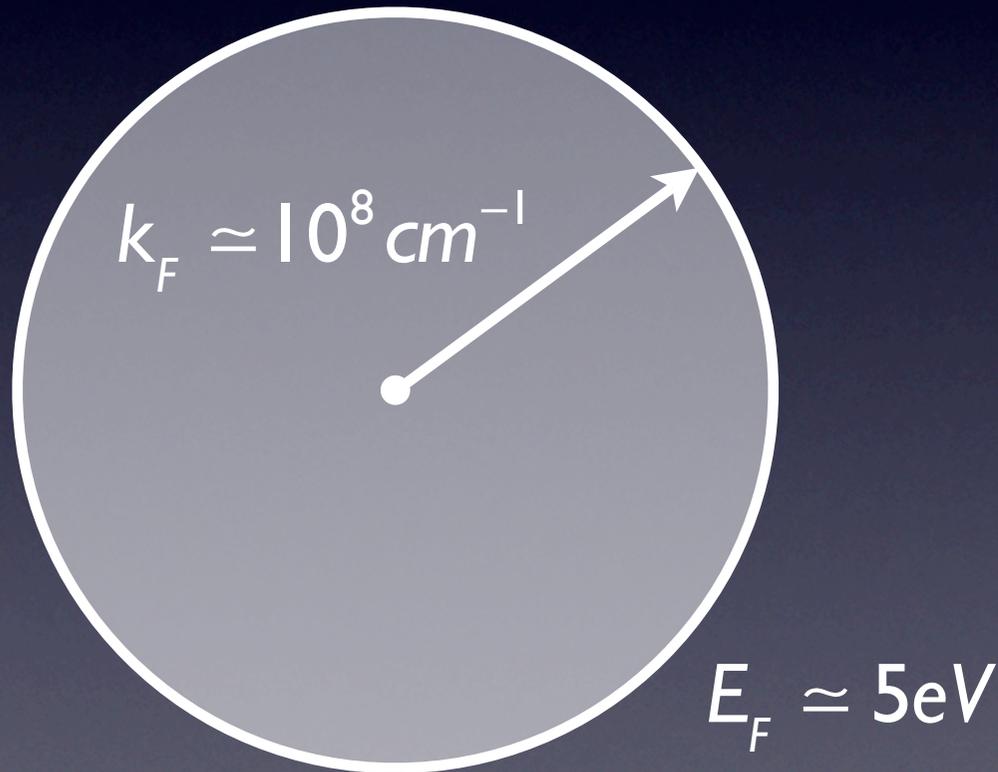
By focusing our attention on them we were able to construct a theory of superconductivity.

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The normal ground state wavefunction is a filled Fermi sphere for both spin directions.

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This huge energy difference contributed to the great difficulty of the problem.

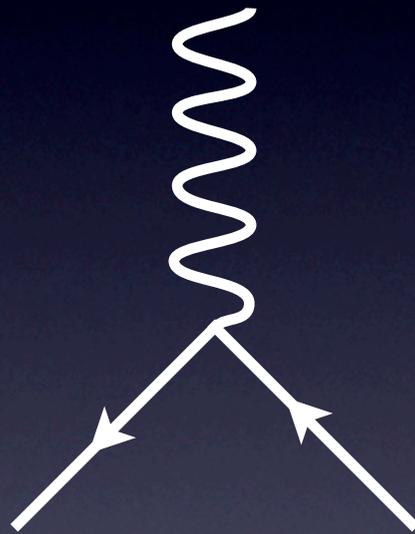
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After the work of Fröhlich, Bardeen and Pines the interaction that produces superconductivity was believed to arise due to phonon exchange which, under some conditions, would be an attractive interaction between electrons near the Fermi surface.

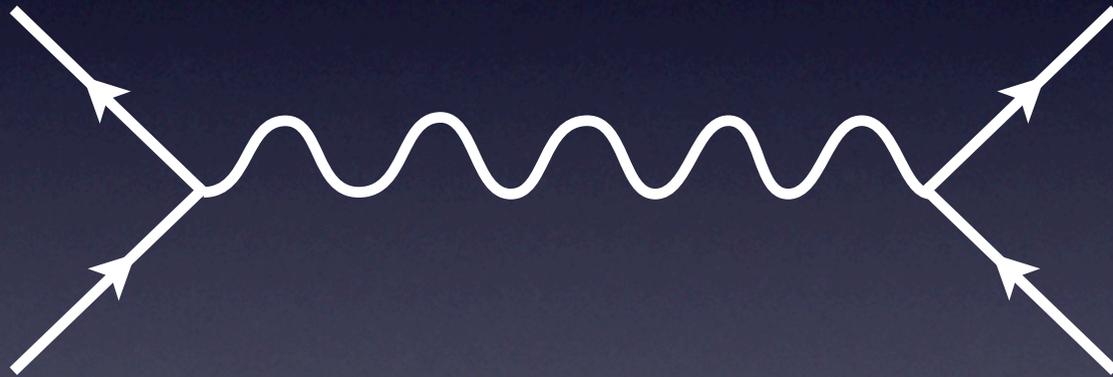
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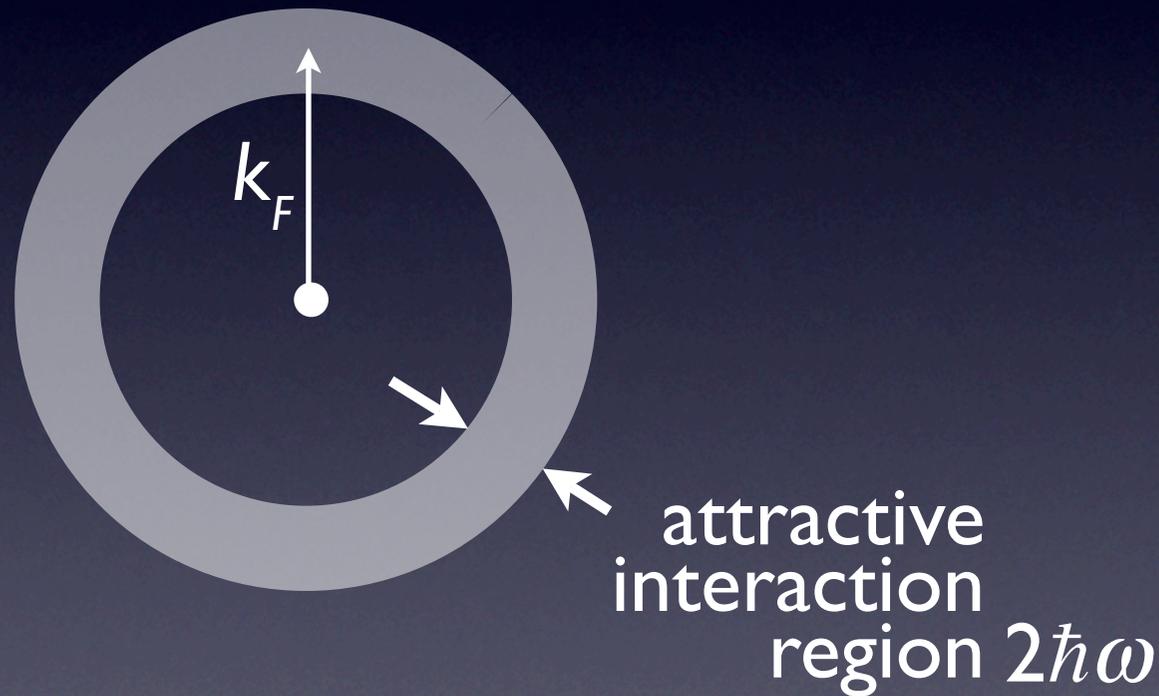
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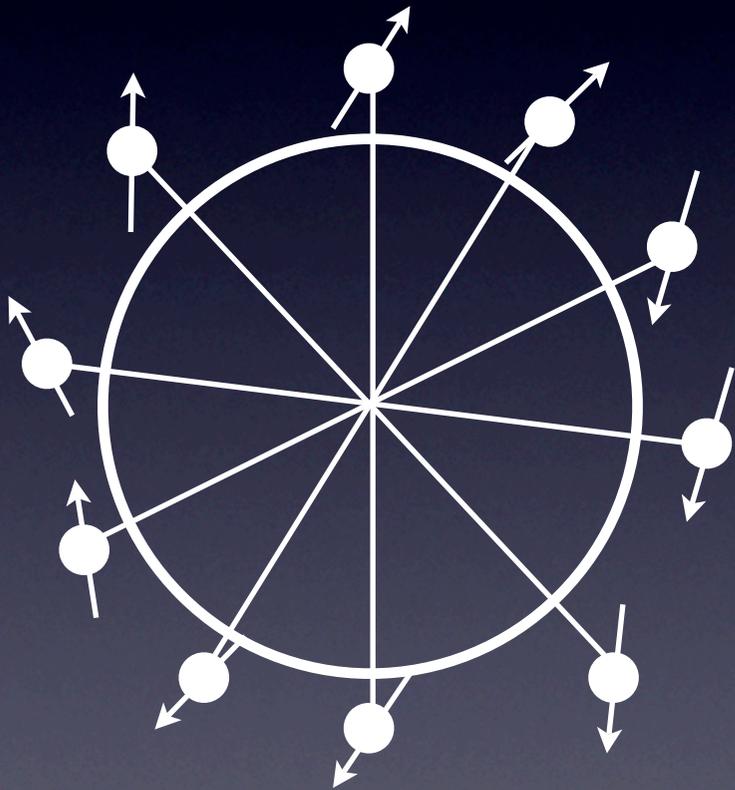
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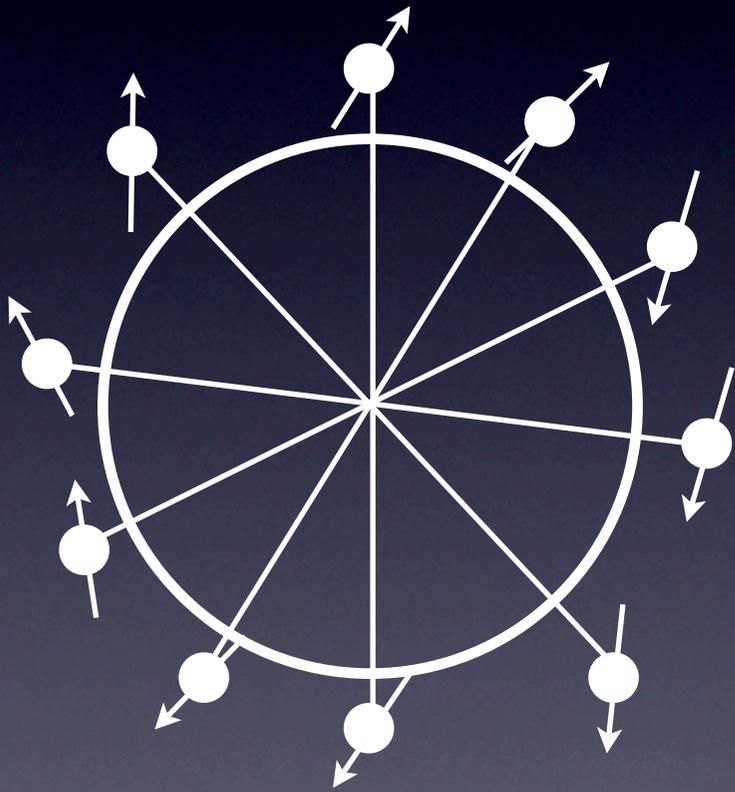
Coherent superpositions of the original states, that are separated from them by a volume independent energy gap, can appear.

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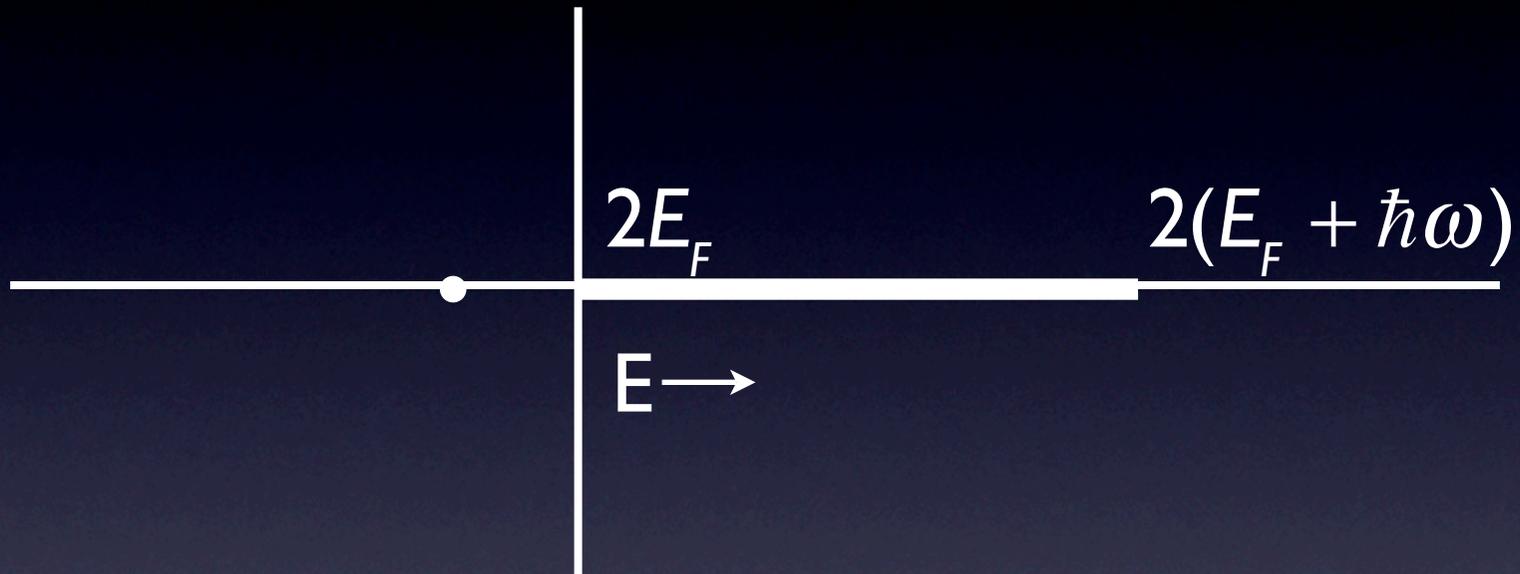
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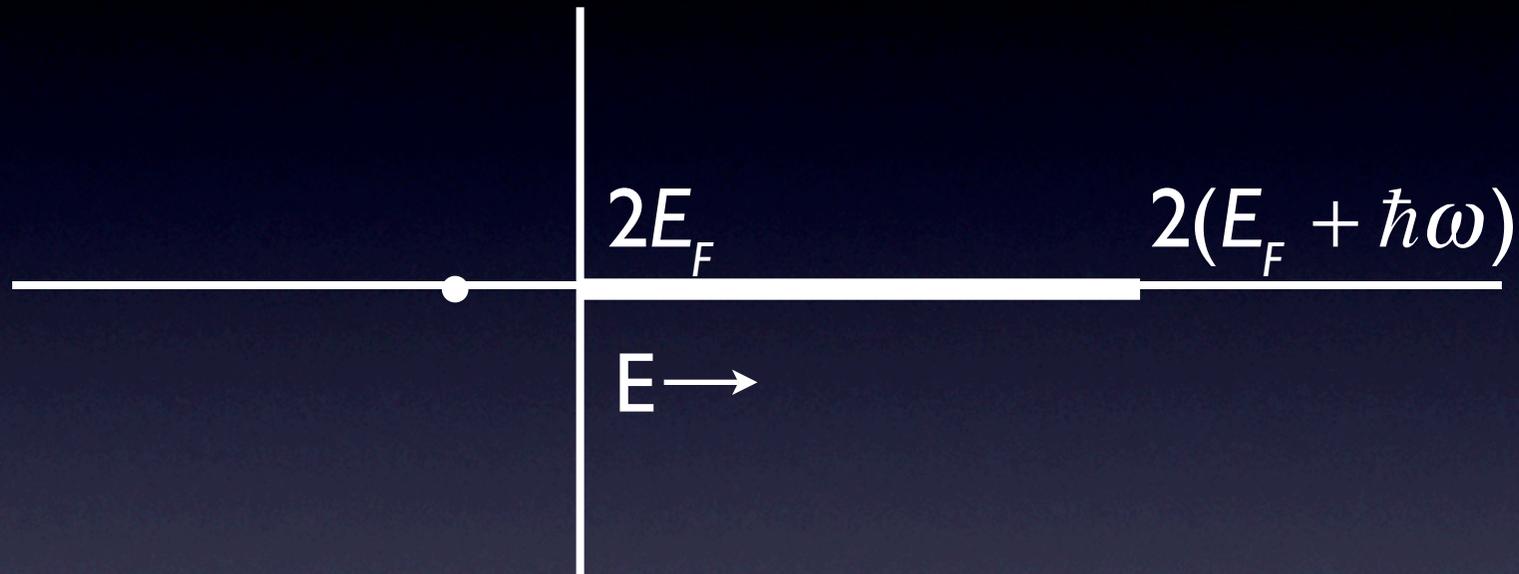
Every such singlet spin zero-momentum pair state can scatter to every other.

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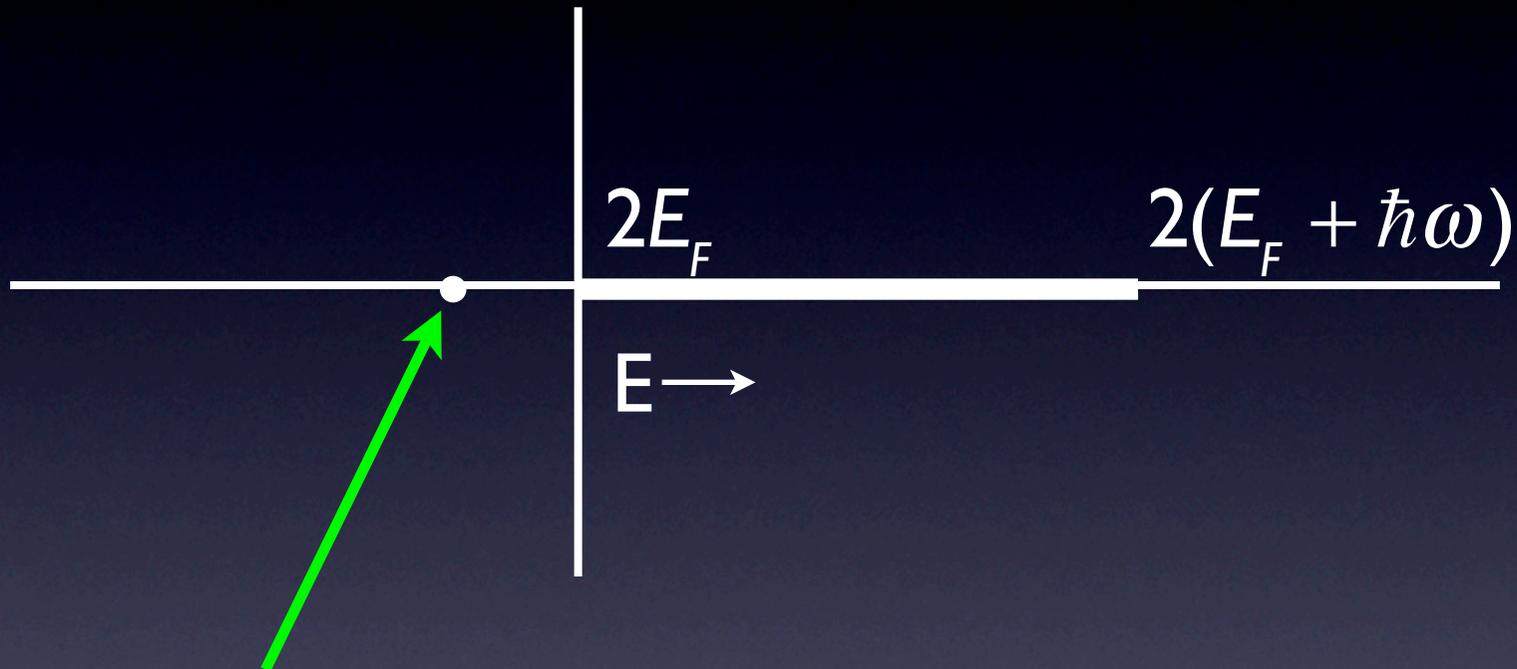


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A single state, which is a coherent superposition of the original states, is separated from the rest by a volume independent energy gap.

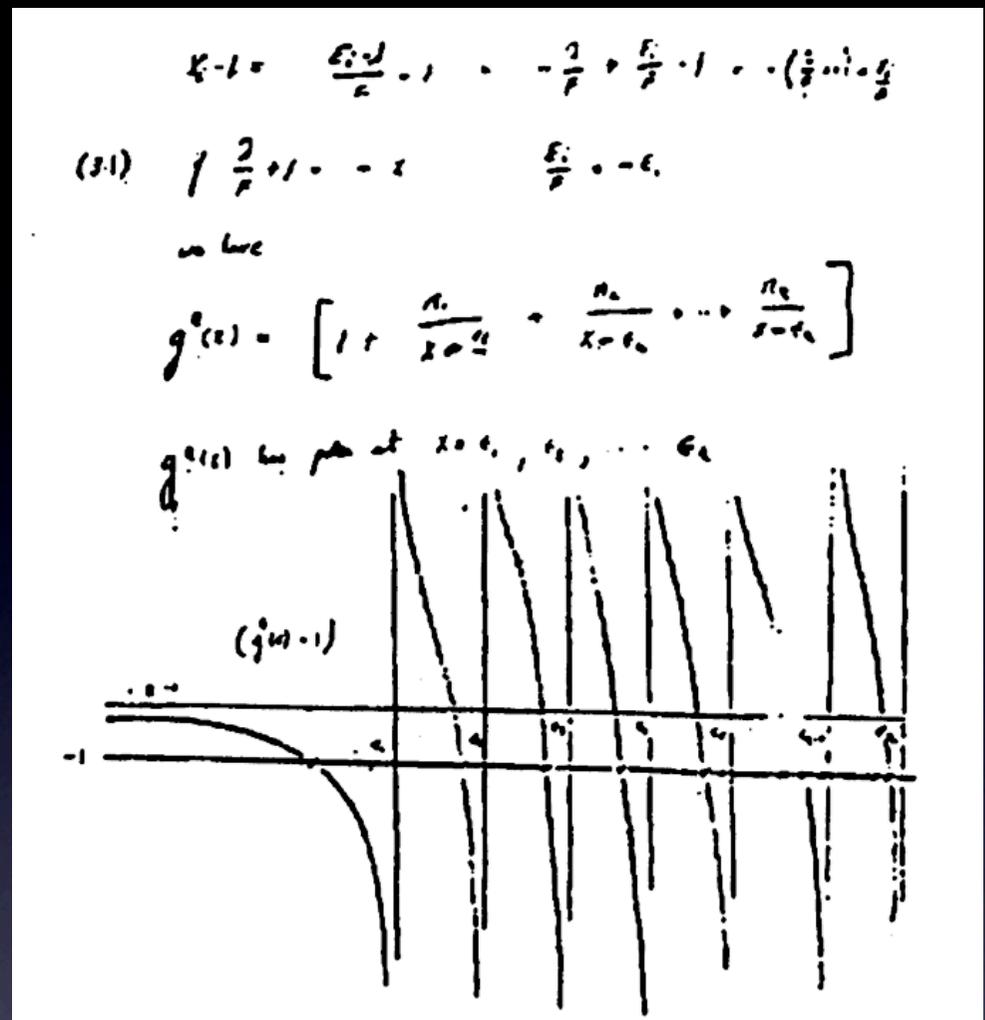
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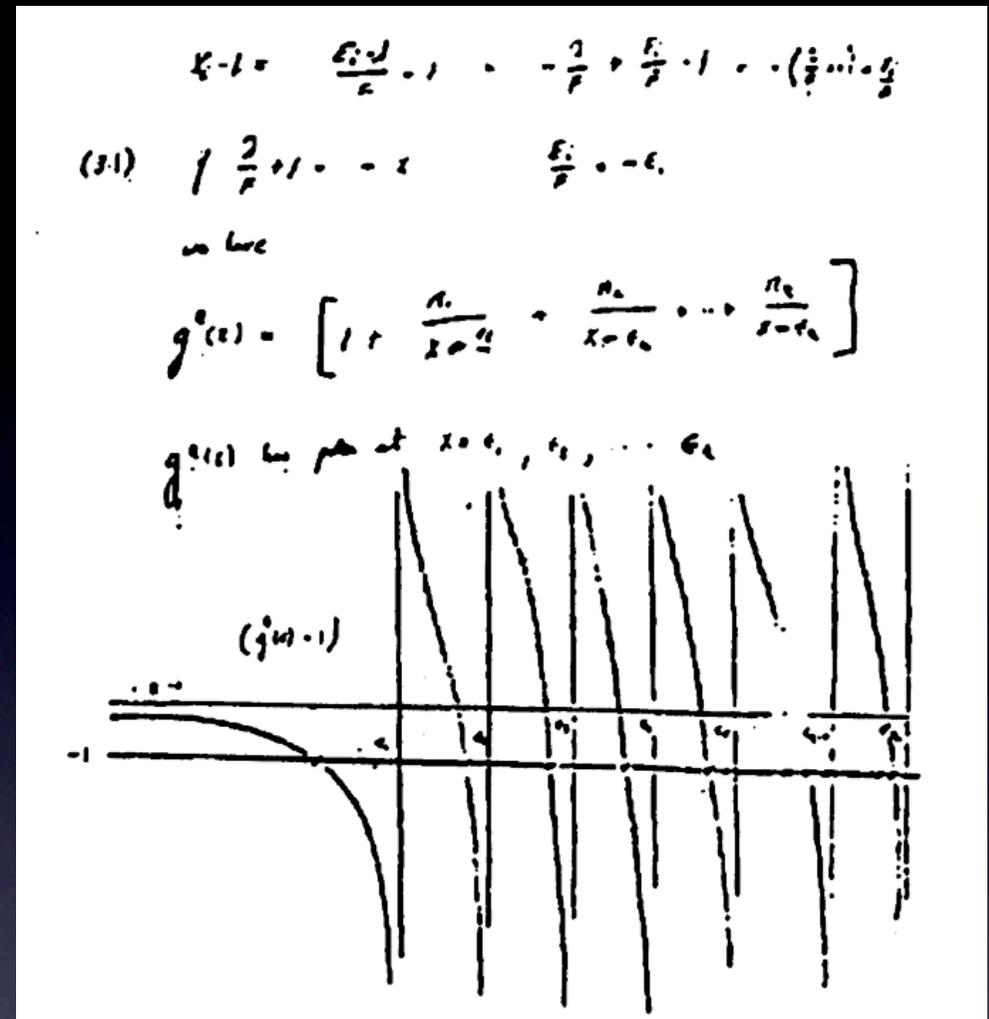
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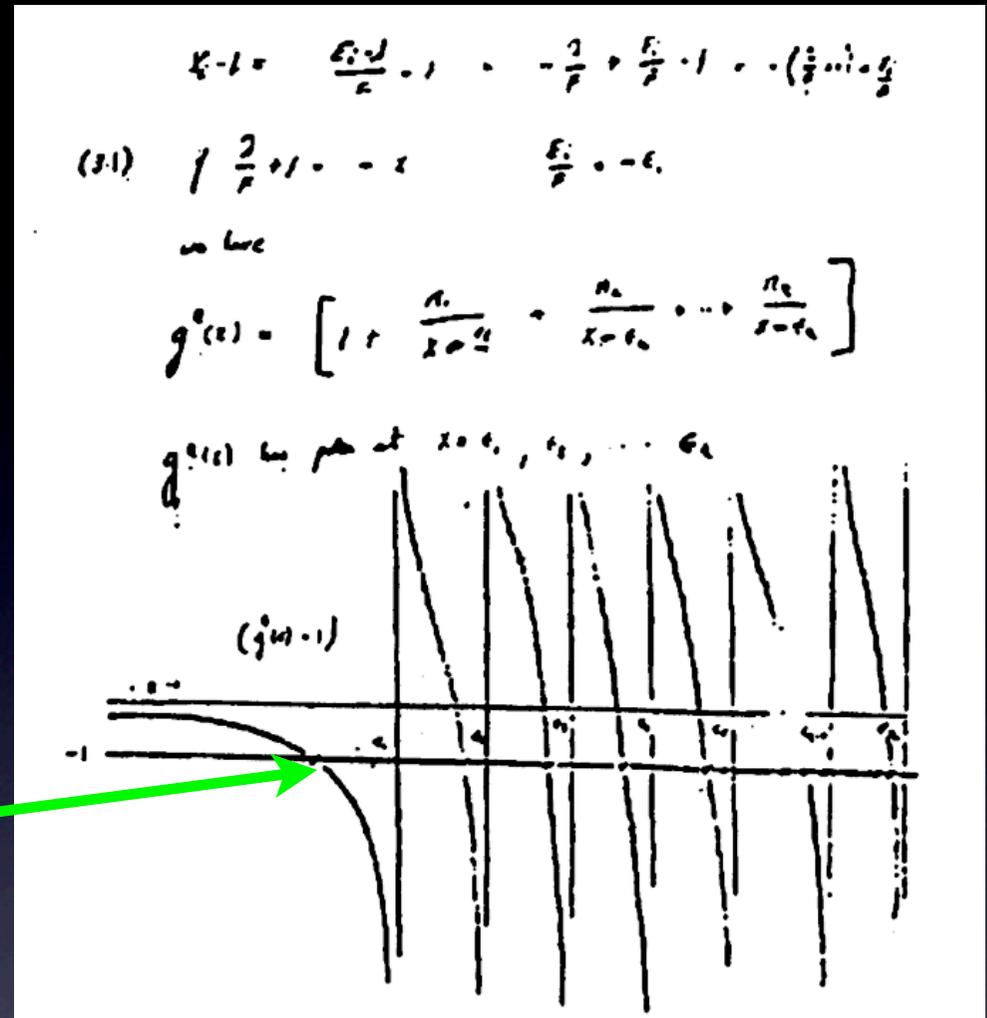
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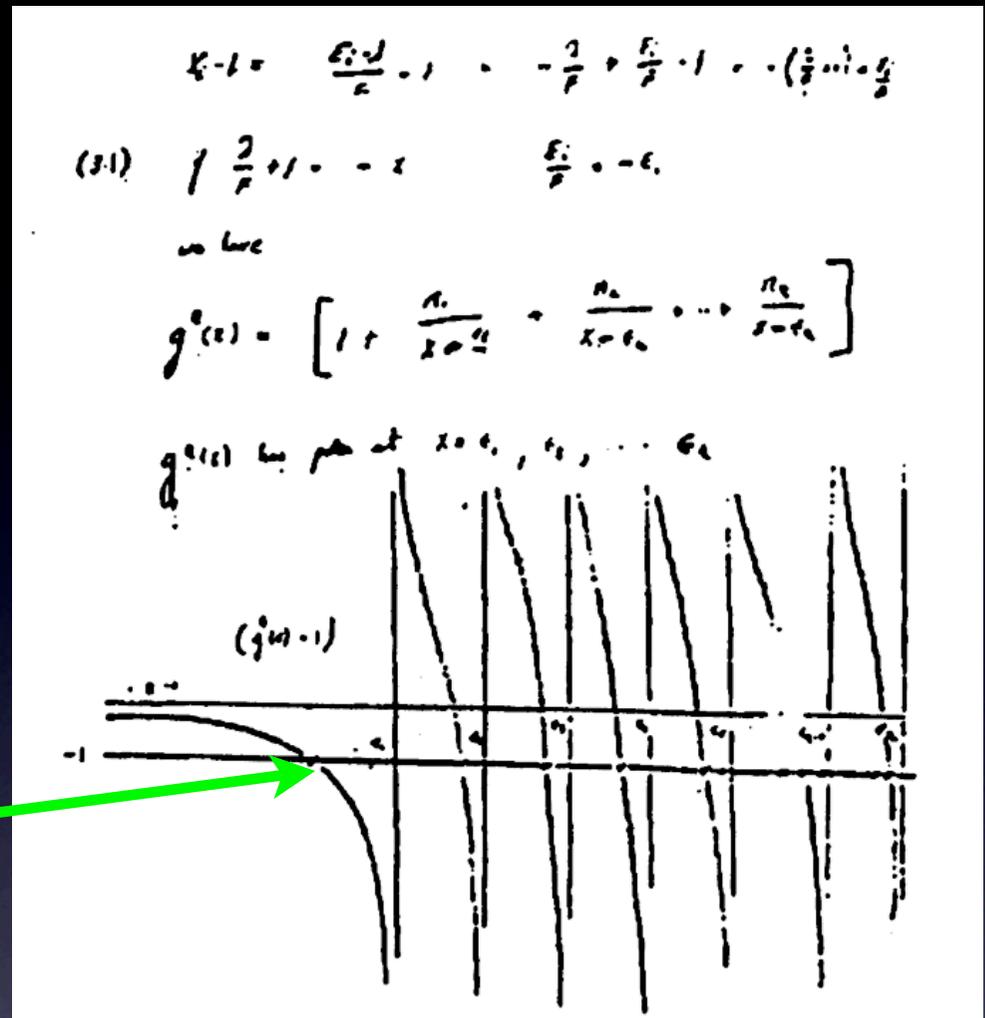
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It is split from the continuum by a volume independent energy gap, displaying, the now well-known, essential singularity in the coupling constant.

$$E - 2E_F = \frac{-2\hbar\omega}{e^{2/N(0)V} - 1}$$

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In addition, the exponential factor seemed to give a natural explanation of why the transition energy into the superconducting state is so small.

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One can estimate that 10^6 to 10^7 pairs occupy the same volume.

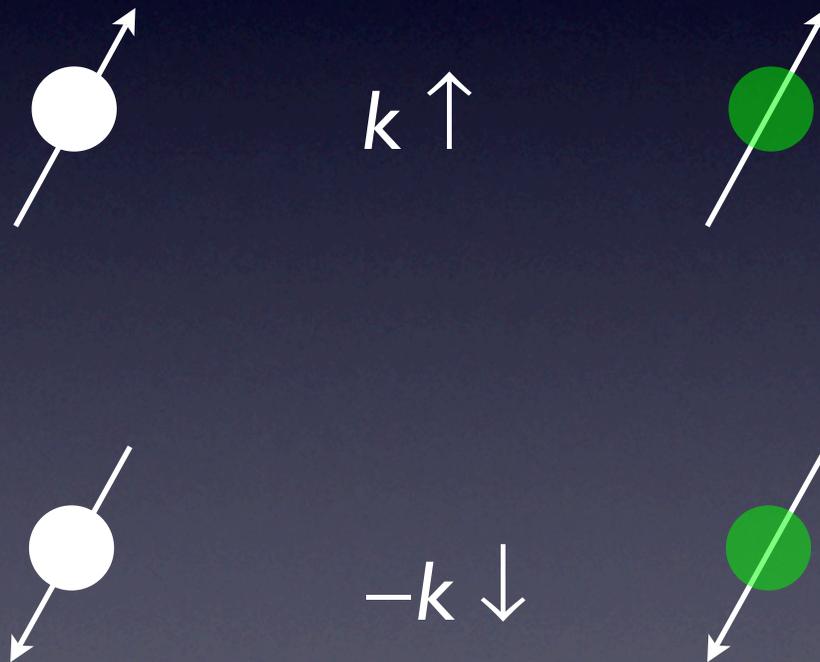
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BCS solves this problem by introducing a wave function that satisfies the Pauli exclusion principle and that contains the many overlapping non-interacting pairs.

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Typically the pair function, $\chi_{\uparrow\downarrow}(r)$, extends $\simeq 10^{-4}$ cm; this has come to be called off-diagonal long range order.

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$$\langle \underline{\psi}_0 | H_{pairing} | \underline{\psi}_0 \rangle$$

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$$\Delta = 2(\hbar\omega)e^{-1/N(0)V}$$

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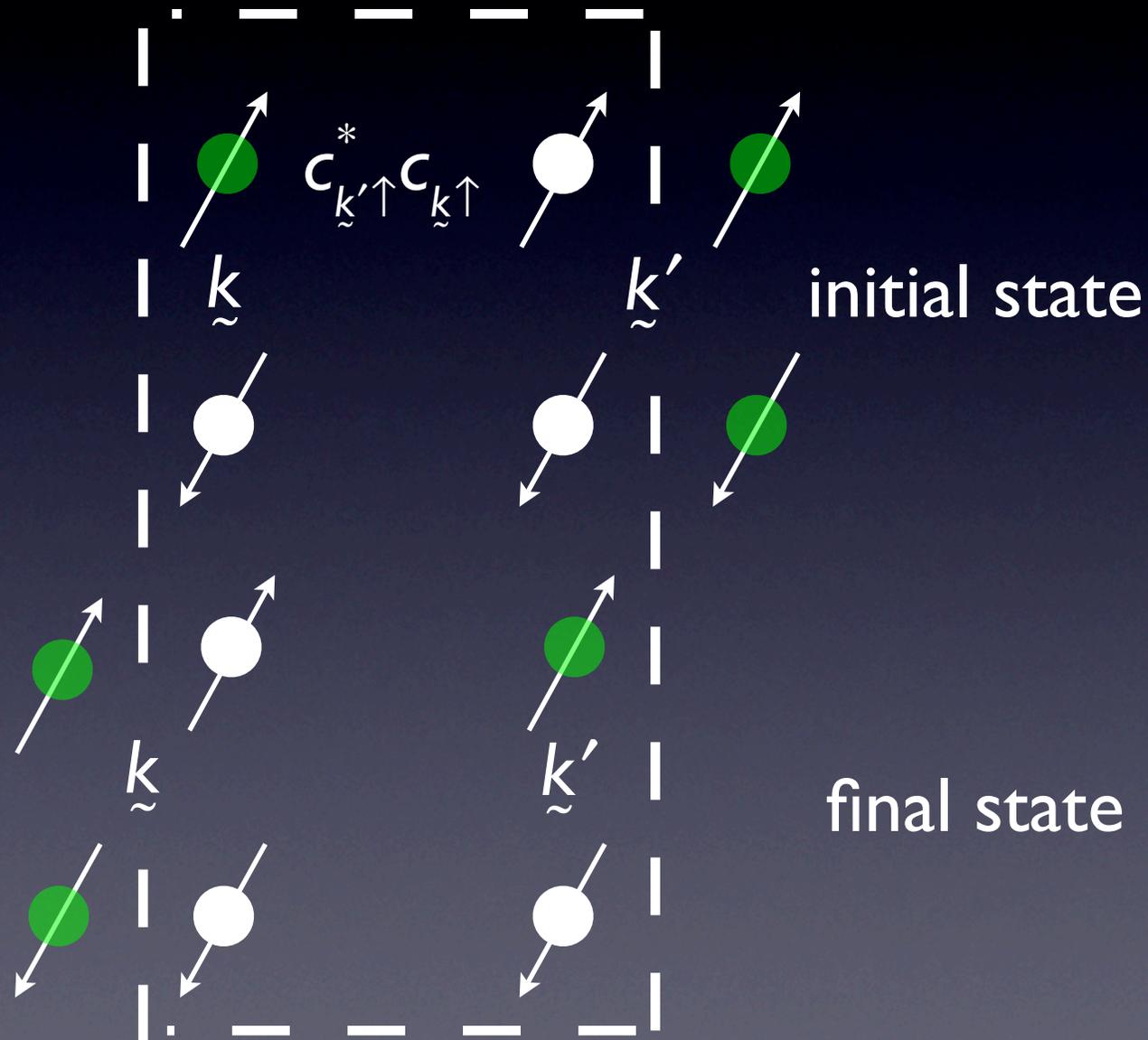
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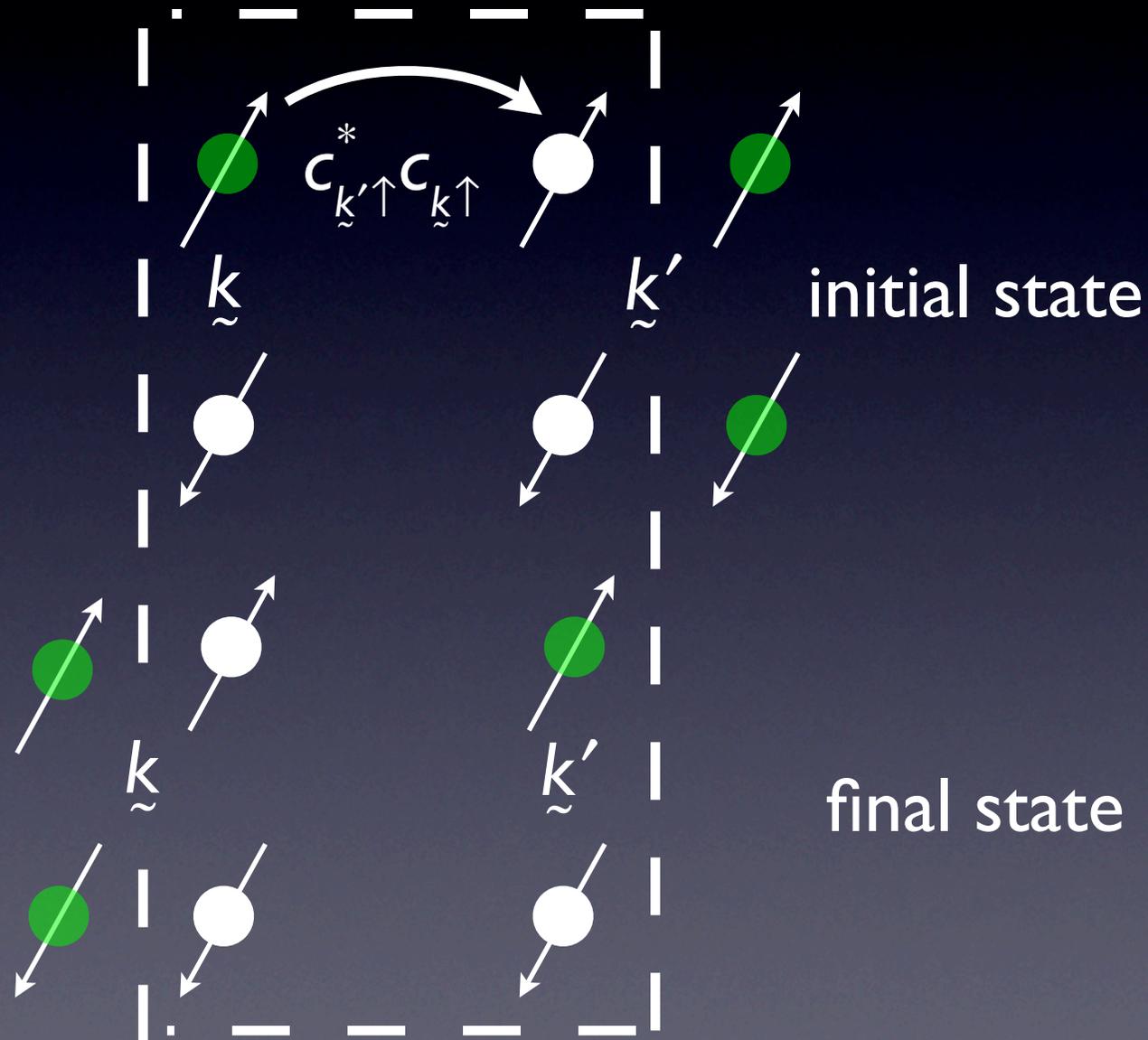
the initial and final states are connected in a new and unexpected way:

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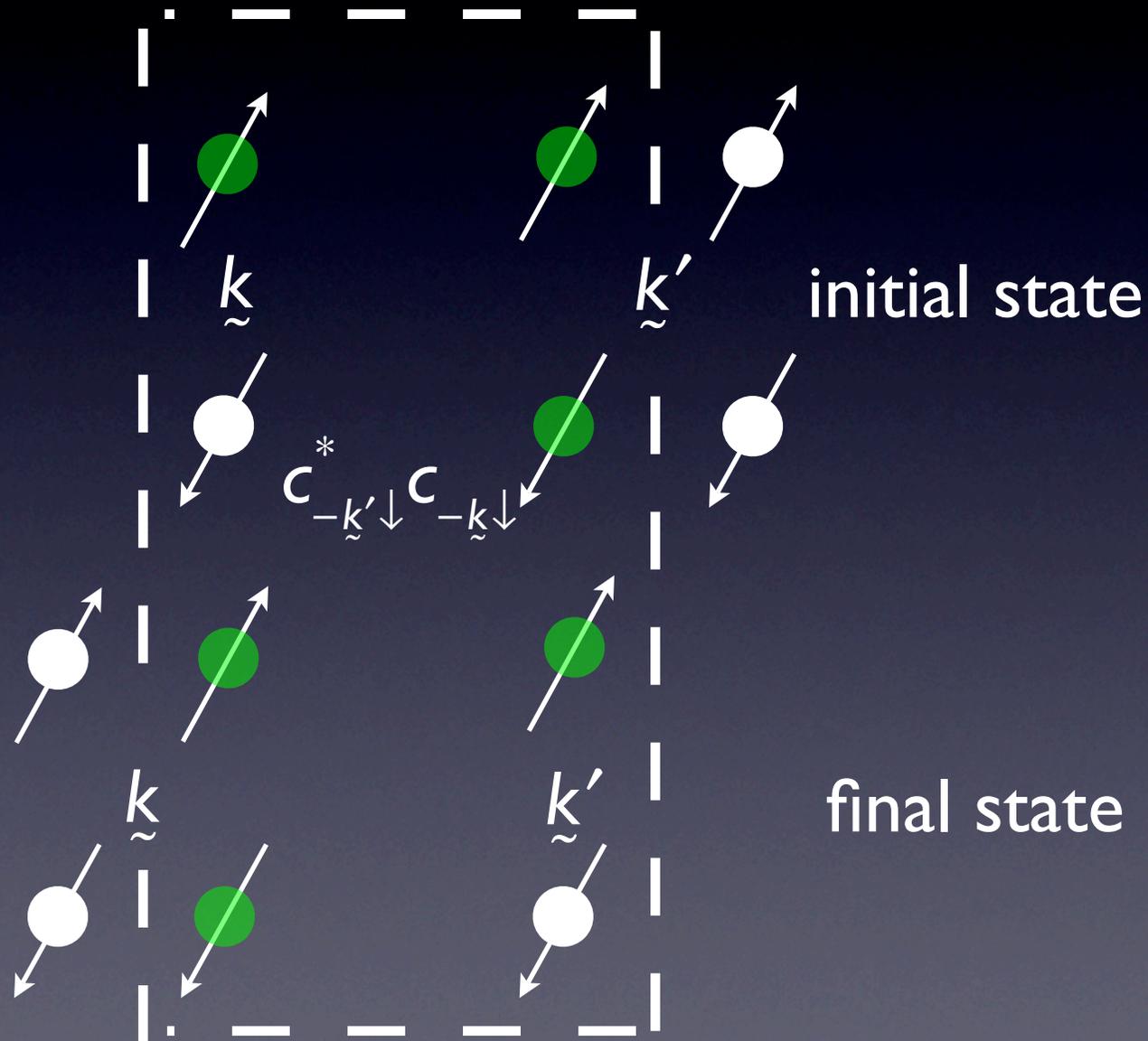


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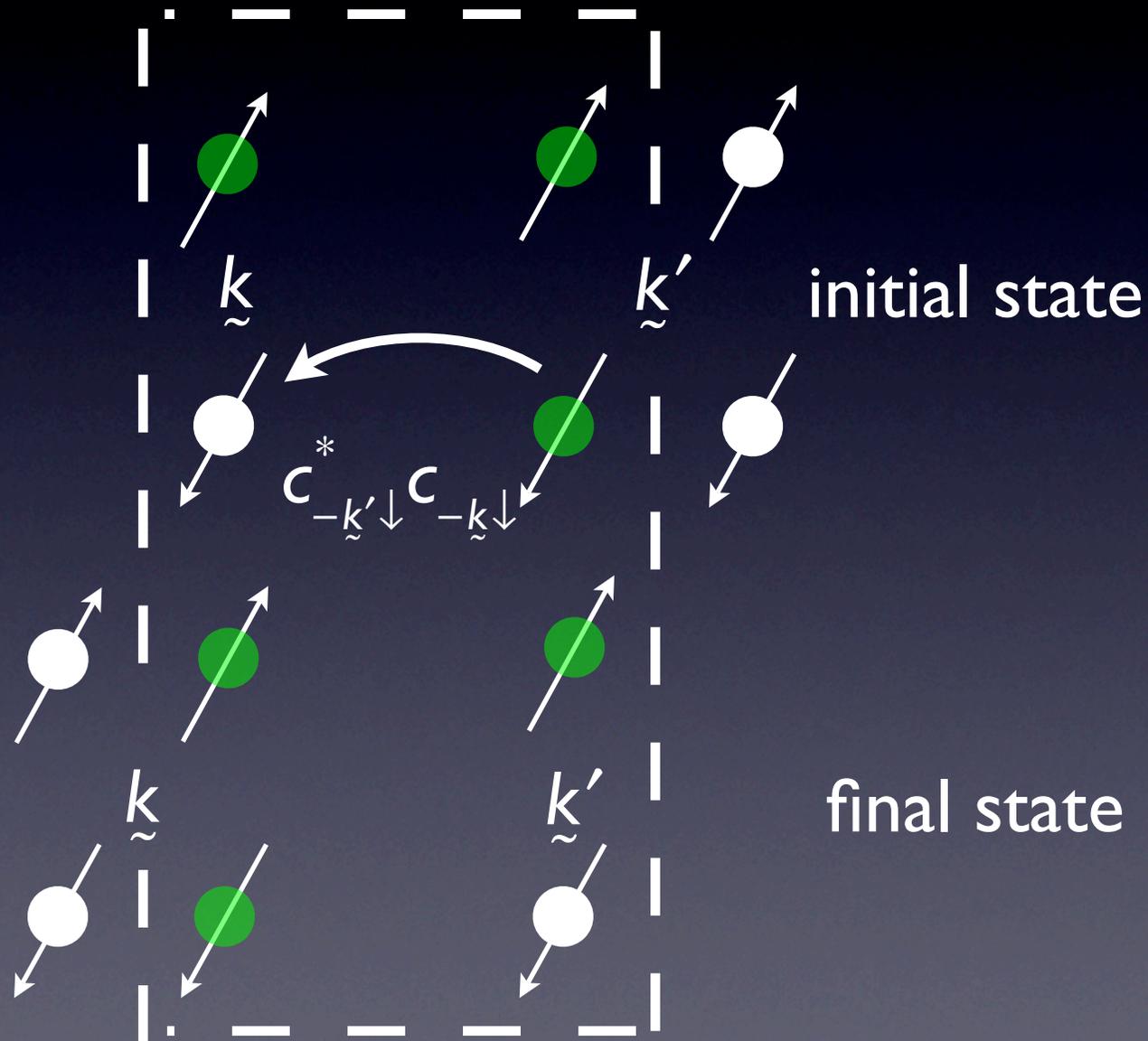


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TABLE II. Matrix elements of single-particle scattering operator.

Wave functions*				Ground (+) or excited (-)	Energy difference $W_i - W_f$	Probability of initial state	Matrix elements	
Initial, Ψ_i ($k\uparrow, -k\downarrow$), ($k'\uparrow, -k'\downarrow$)		Final, Ψ_f ($k\uparrow, -k\downarrow$), ($k'\uparrow, -k'\downarrow$)					k	k'
(a)								
X0	00	00	X0	+	+	$\frac{1}{2}s(1-s'-p')$	$[(1-h)(1-h')]^{\frac{1}{2}}$	$-(hh')^{\frac{1}{2}}$
X0	XX	XX	X0	-	-	$\frac{1}{2}s p'$	$(hh')^{\frac{1}{2}}$	$-[(1-h)(1-h')]^{\frac{1}{2}}$
				+	-	$\frac{1}{2}s p'$	$-[(1-h)h']^{\frac{1}{2}}$	$-[h(1-h')]^{\frac{1}{2}}$
				-	+	$-(E+E')$	$-\frac{1}{2}s(1-s'-p')$	$-[h(1-h')]^{\frac{1}{2}}$
(b)								
XX	0X	0X	XX	+	+	$\frac{1}{2}s'(1-s-p)$	$(hh')^{\frac{1}{2}}$	$-[(1-h)(1-h')]^{\frac{1}{2}}$
00	0X	0X	00	-	-	$\frac{1}{2}s' p$	$[(1-h)(1-h')]^{\frac{1}{2}}$	$-(hh')^{\frac{1}{2}}$
				+	-	$-(E+E')$	$[\frac{1}{2}s'(1-s-p)]^{\frac{1}{2}}$	$[h'(1-h)]^{\frac{1}{2}}$
				-	+	$E+E'$	$[\frac{1}{2}s' p]^{\frac{1}{2}}$	$[h(1-h')]^{\frac{1}{2}}$
(c)								
X0	0X	00	XX	+	+	$\frac{1}{2}ss'$	$[(1-h)h']^{\frac{1}{2}}$	$[h(1-h')]^{\frac{1}{2}}$
		XX	00	-	-	$\frac{1}{2}ss'$	$-[h(1-h')]^{\frac{1}{2}}$	$-[h'(1-h)]^{\frac{1}{2}}$
				+	-	$E-E'$	$[(1-h)(1-h')]^{\frac{1}{2}}$	$-(hh')^{\frac{1}{2}}$
				-	+	$E'-E$	$-(hh')^{\frac{1}{2}}$	$[(1-h)(1-h')]^{\frac{1}{2}}$
(d)								
XX	00	0X	X0	+	+	$-(E+E')$	$(1-s-p)(1-s'-p')$	$[h(1-h')]^{\frac{1}{2}}$
00	XX			-	-	$E+E'$	pp'	$-[(1-h)h']^{\frac{1}{2}}$
				+	-	$E'-E$	$(1-s-p)p'$	$-(hh')^{\frac{1}{2}}$
				-	+	$E-E'$	$p(1-s'-p')$	$[(1-h)(1-h')]^{\frac{1}{2}}$

* For transitions which change spin, reverse designations of ($k'\uparrow, -k'\downarrow$) in the initial and in the final states.

The superposition of these two amplitudes results in strikingly different behavior for interactions depending on how they transform under time reversal.

In time reversal the coordinates transform as

$$x \rightarrow x$$

$$y \rightarrow y$$

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while various operators transform as

$$j(r, t) \rightarrow -j(r, -t)$$

$$\rho(r, t) \rightarrow +\rho(r, -t)$$

$$\sigma_z(t) \rightarrow -\sigma_z(-t)$$

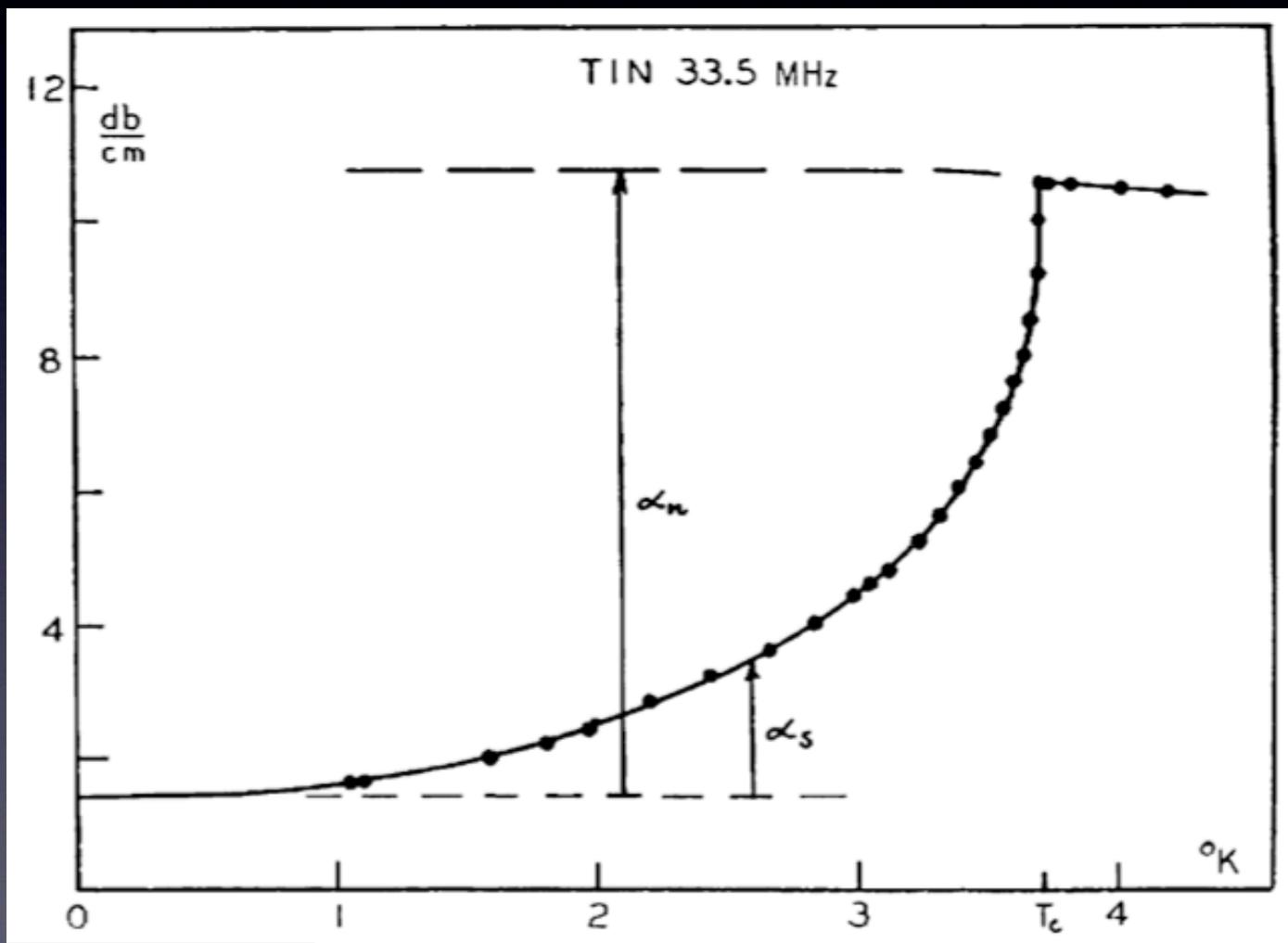
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Nuclear spin relaxation involves σ

Ultrasonic attenuation, as a function of temperature, falls off very rapidly across the superconducting transition.

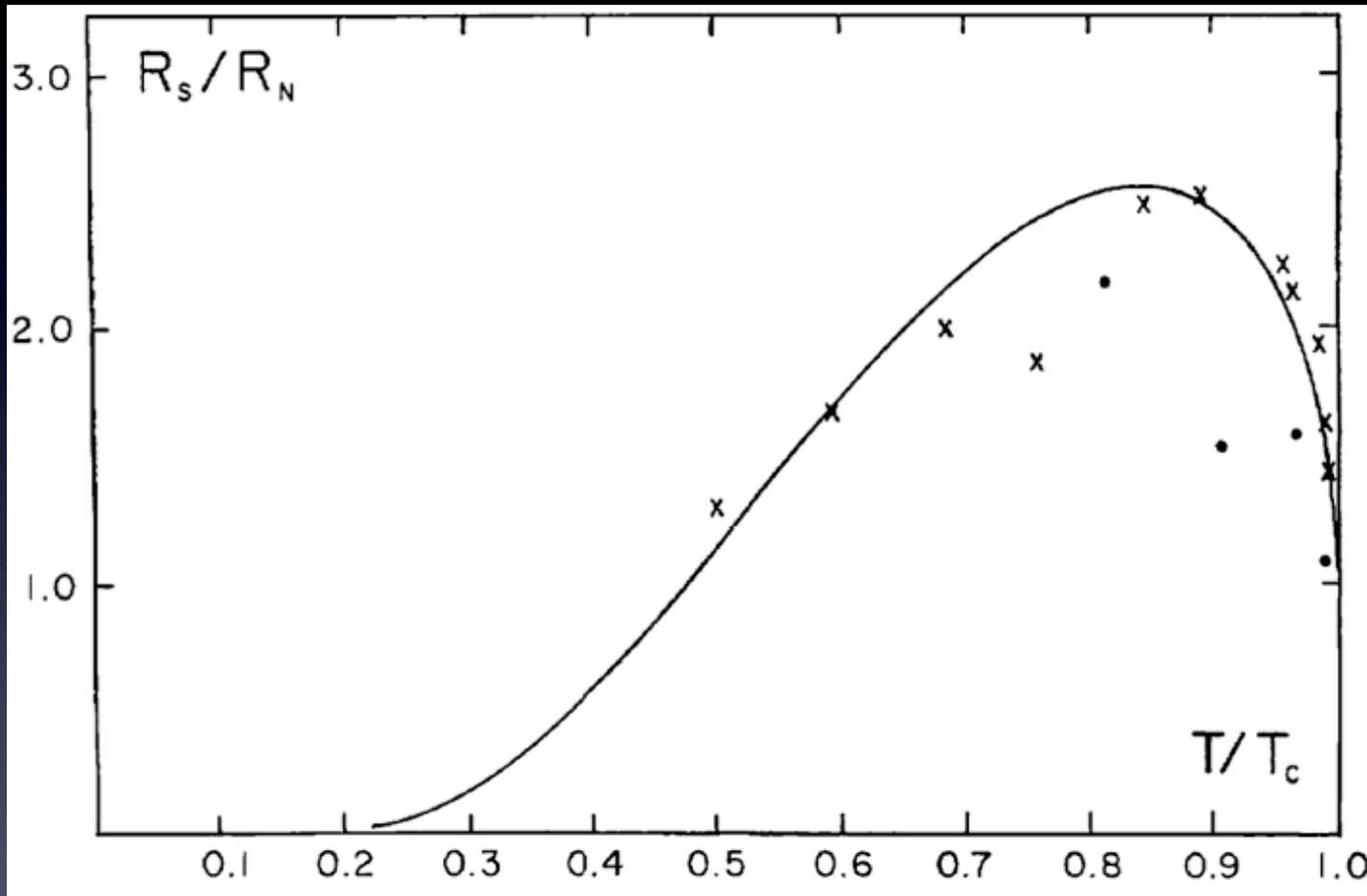
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Morse and Bohm (1957)

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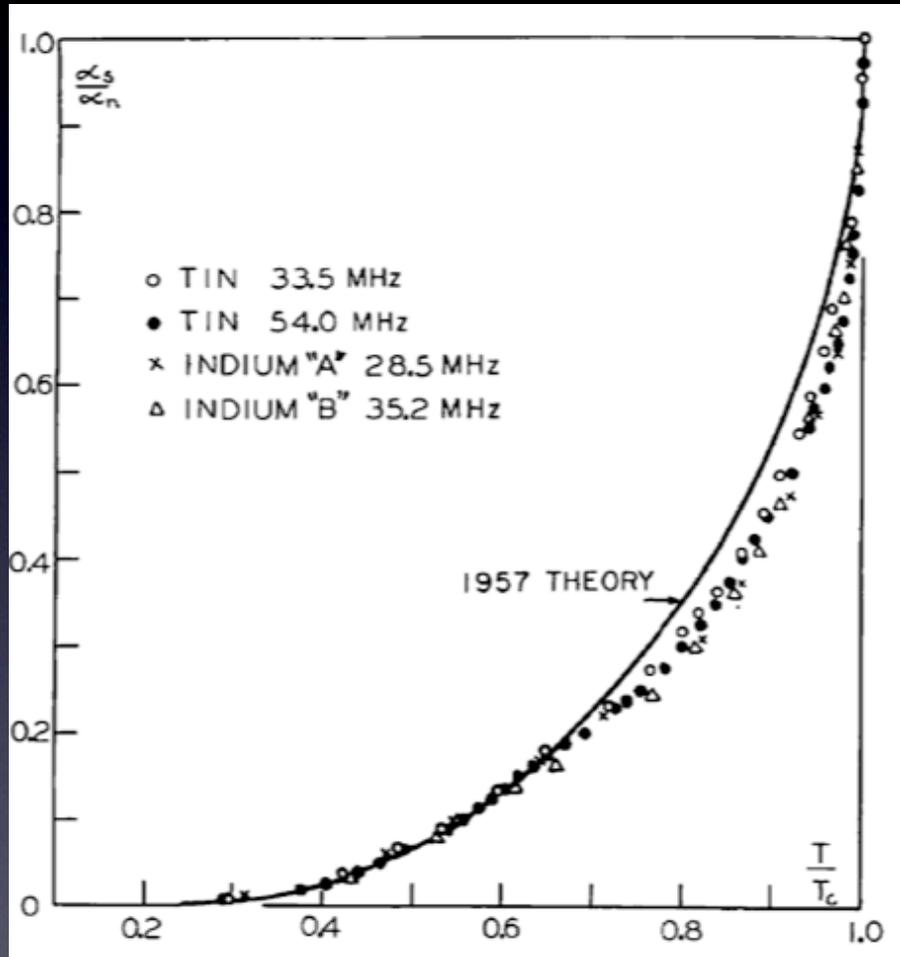


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Comparison with the BCS theory

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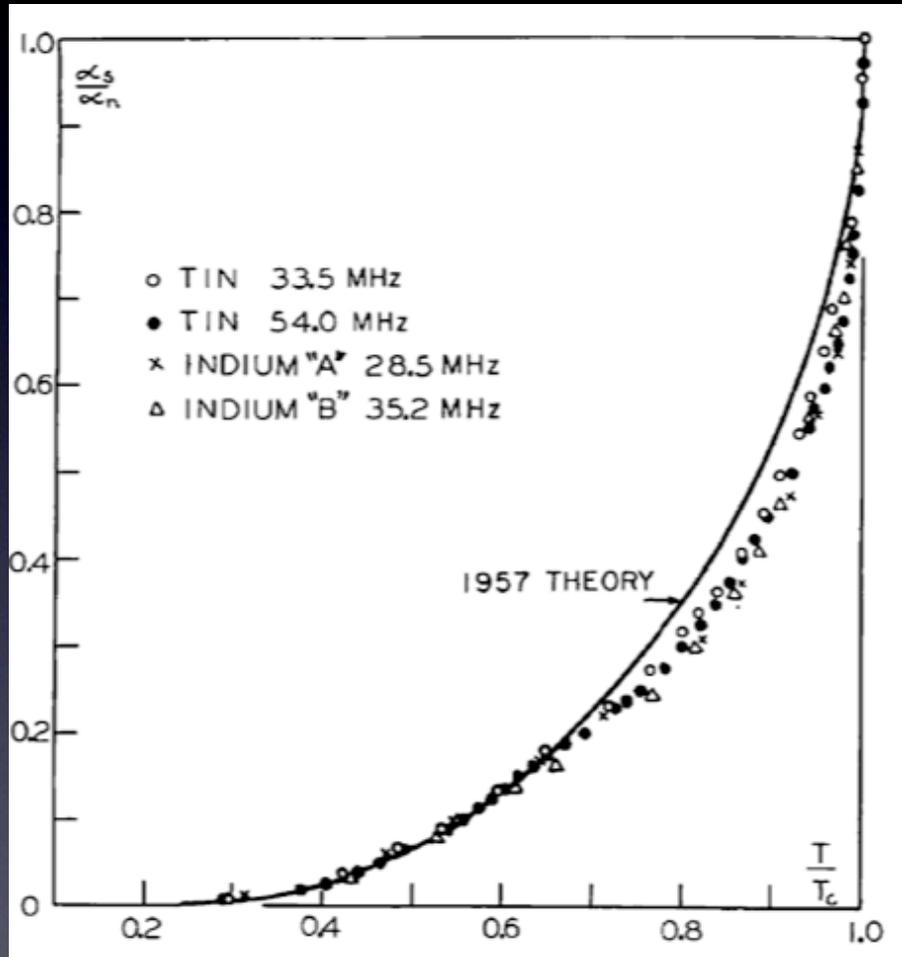
Ultrasonic Attenuation



Data from Morse and Bohm (1957)

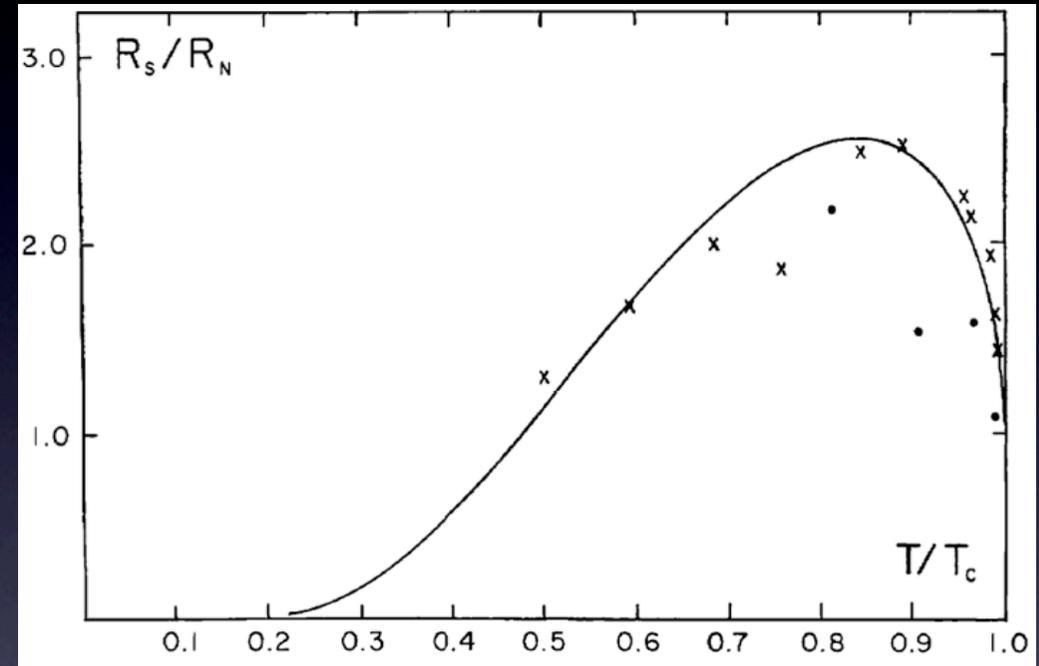
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Nuclear Spin Relaxation



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“...such a striking phenomenon as superconductivity [was] ... nothing more exciting than a footling small interaction between atoms and lattice vibrations.”

Since 1957 the situation has become richer and much more complex.

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I can mention just a few:

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Pairing in:

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Color superconductivity in dense quark matter

Transition Between Bose Einstein and BCS Condensation

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so that a transition between a Bose Einstein and a BCS condensation can be seen.

The broken symmetry displayed by the BCS pair function (the order parameter of the Ginsburg-Landau theory)

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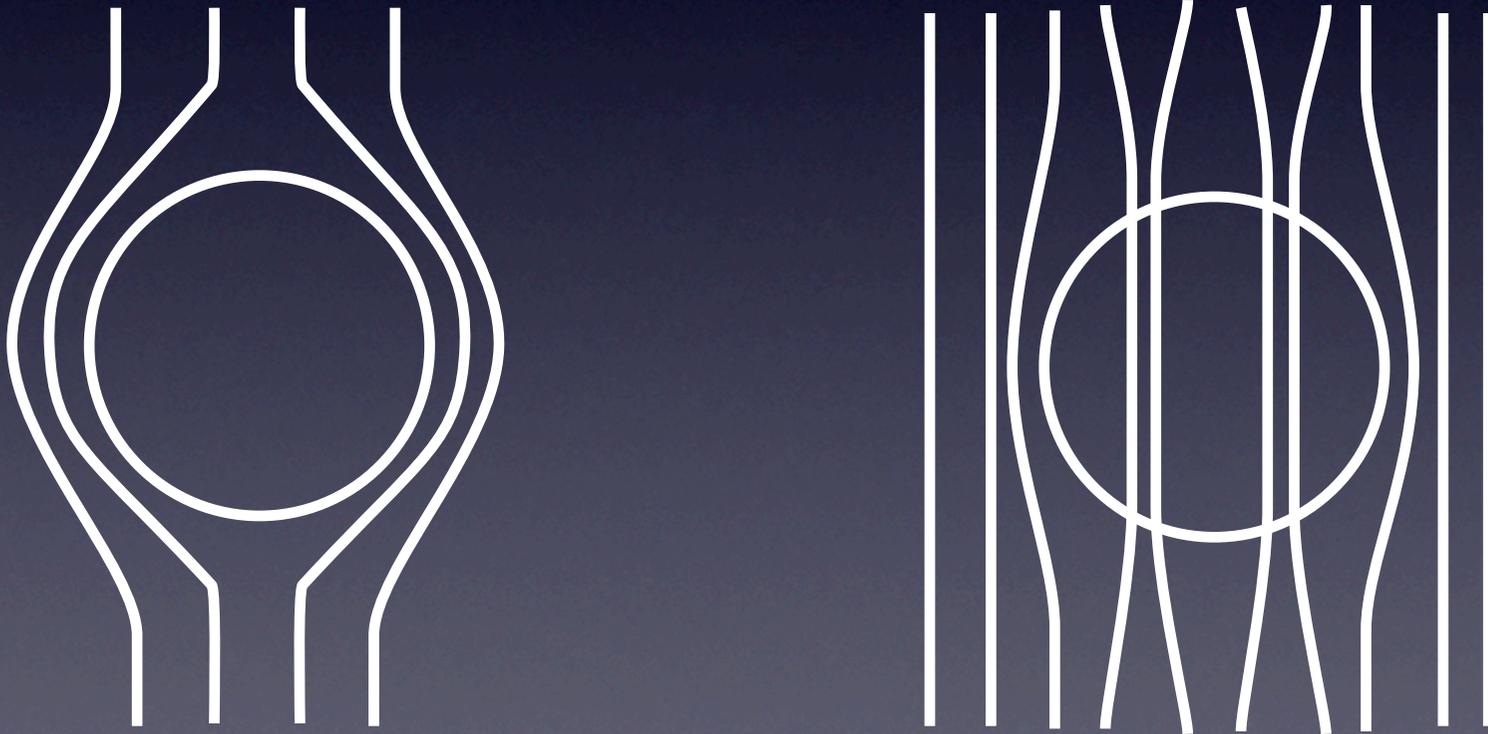
Type II Superconductors

Type II Superconductors

In some situations, it is energetically favorable for a magnetic field to partially penetrate a superconductor breaking it up into many superconducting and normal regions.

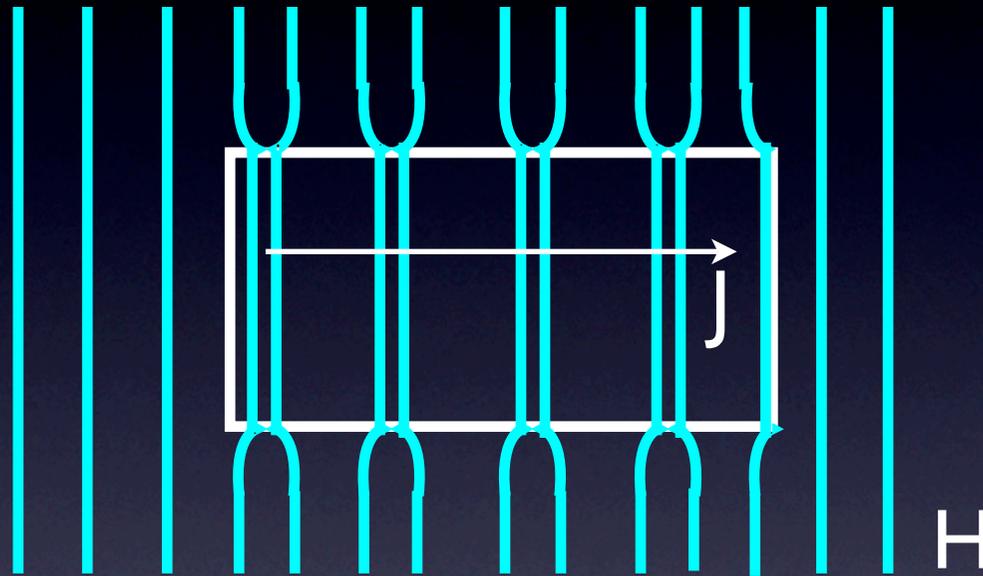
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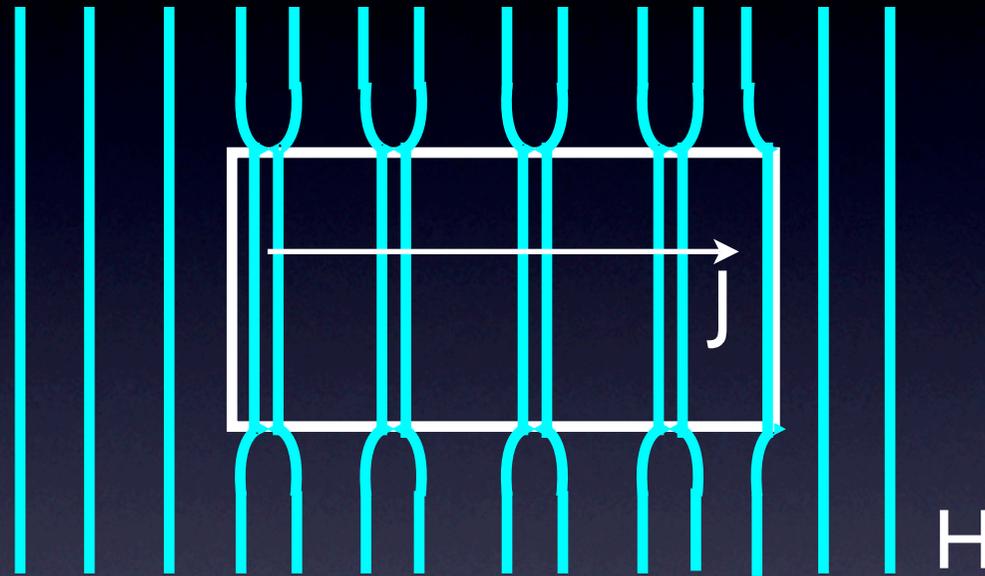


Type II superconductors have been developed that can carry high currents as well as sustain very large magnetic fields.

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Some commonly used materials for both civilian and military applications are niobium-tin and niobium-titanium. Niobium-titanium is often chosen because of its superior mechanical properties. It has a critical magnetic field of 15 Tesla and a critical temperature of 10 K.

Among the many applications:

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Magnetic Resonance Imaging



Japanese superconducting magnetically levitated train



Superconducting magnet used to detonate mines

Many other military and civilian applications are either contemplated or in use:

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High energy accelerators and detectors

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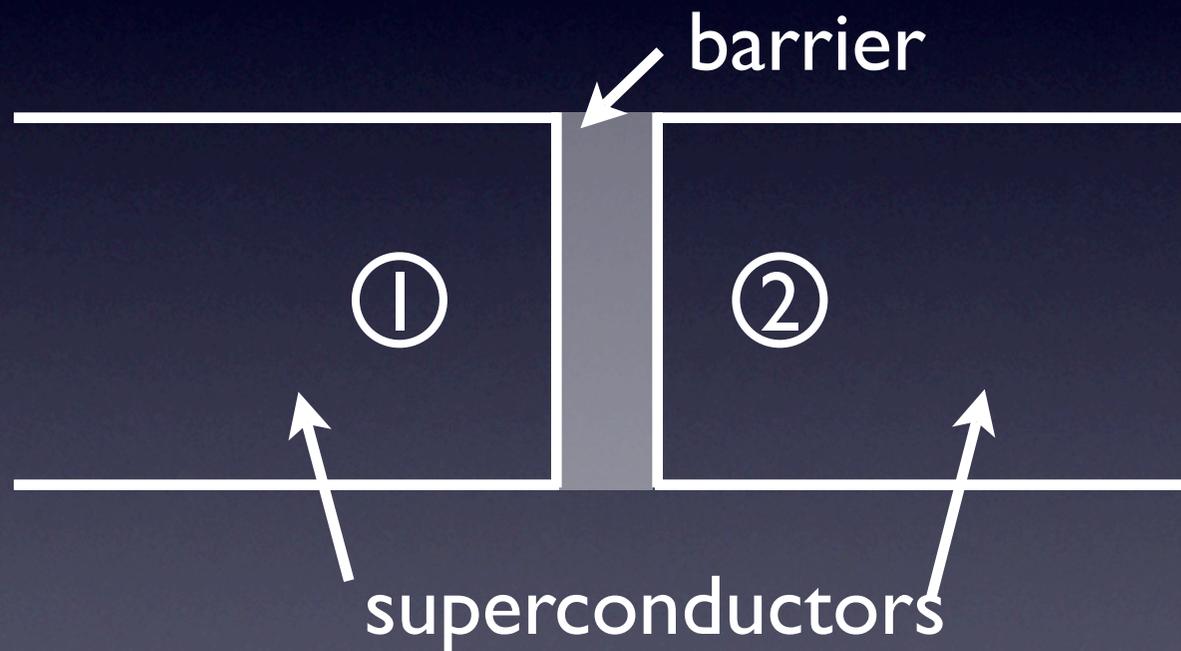
Superconductor Electronics

Superconductor Electronics

Josephson Junctions

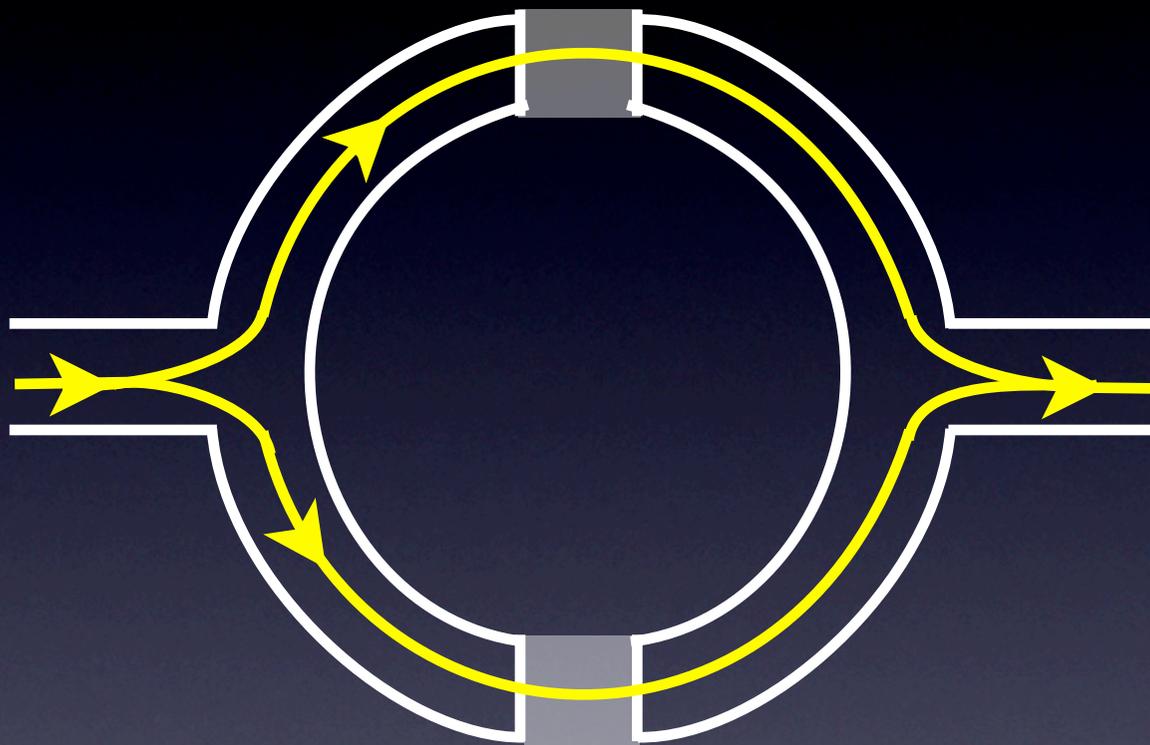
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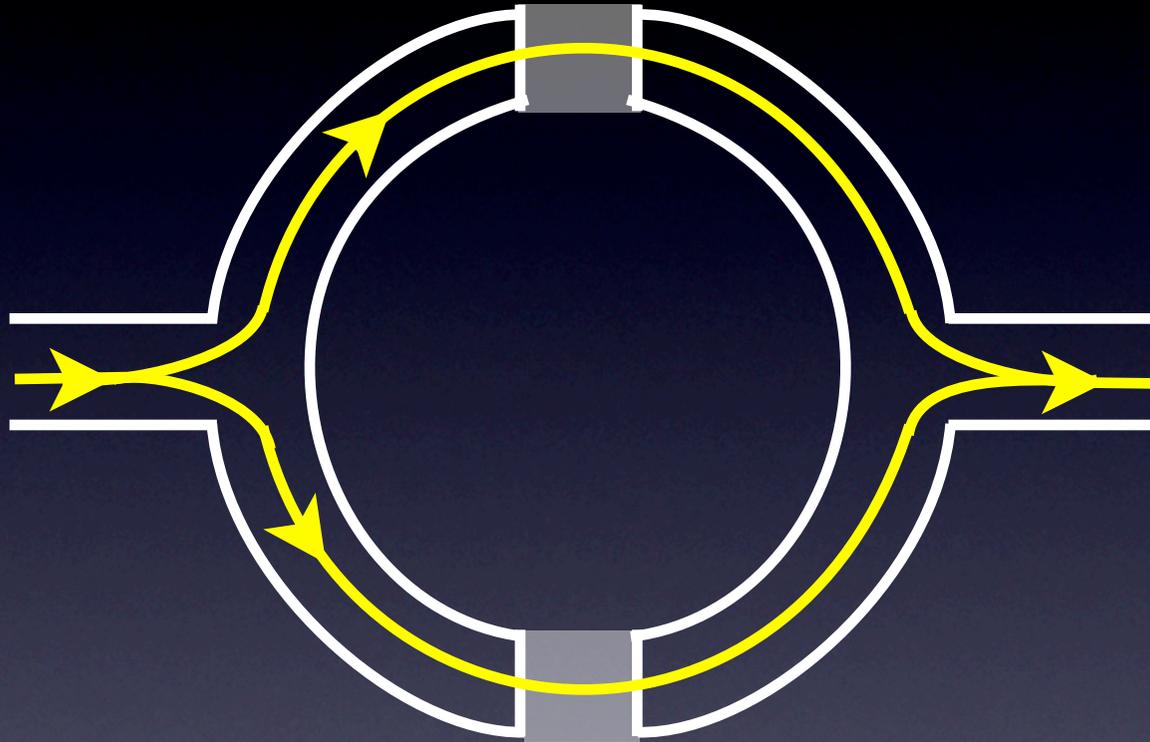


Superconducting Quantum Interference Devices (SQUIDS)

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Very sensitive measurement of magnetic fields

Numerous civilian and military applications

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Submarine detection

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Submarine detection

Oil prospecting

Numerous civilian and military applications

Submarine detection

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Precision sensors in scientific experiments

Numerous civilian and military applications

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Precision sensors in scientific experiments

Gravity waves

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Medical diagnostics

SQUID Superconducting Quantum Interference Device in a medical application

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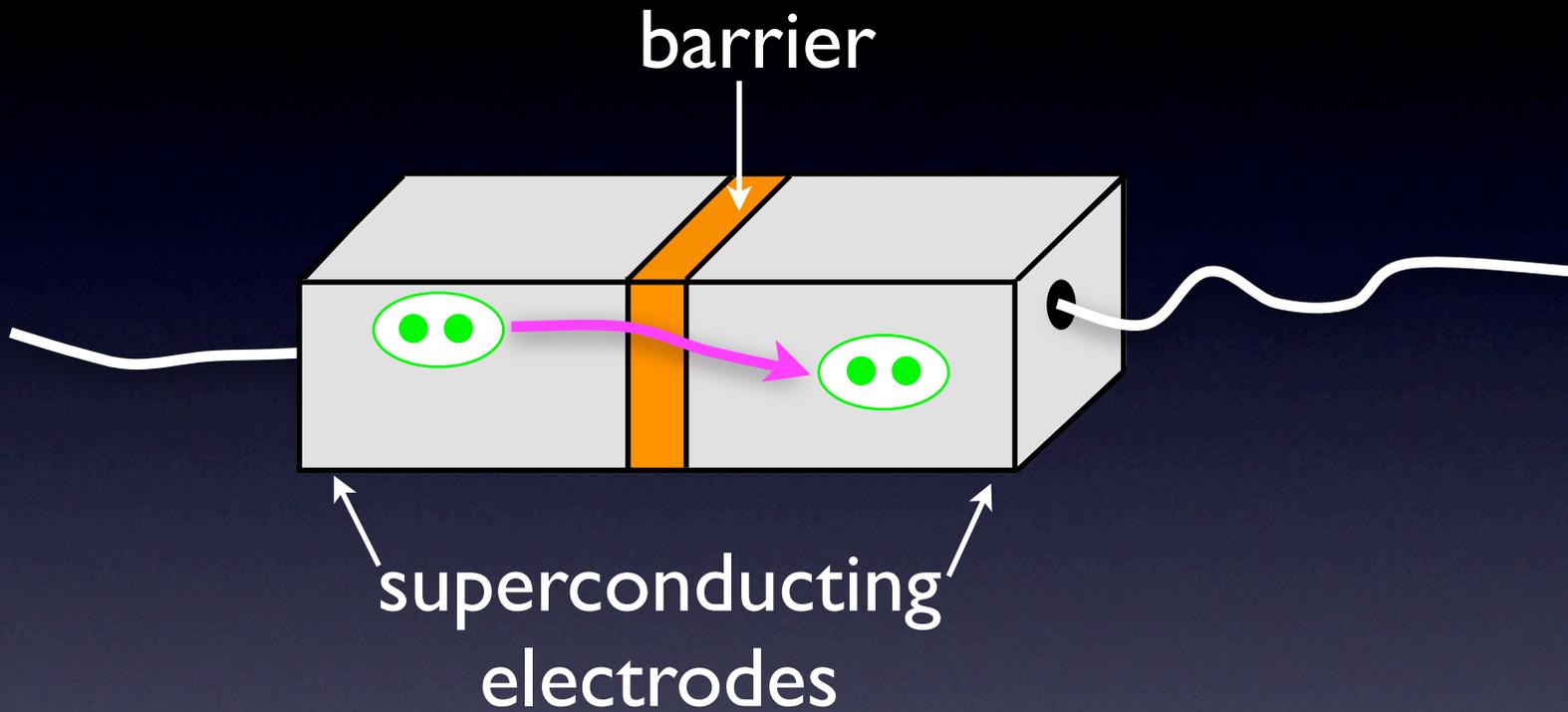
Quantum Computing

Quantum Computing

Single pair box

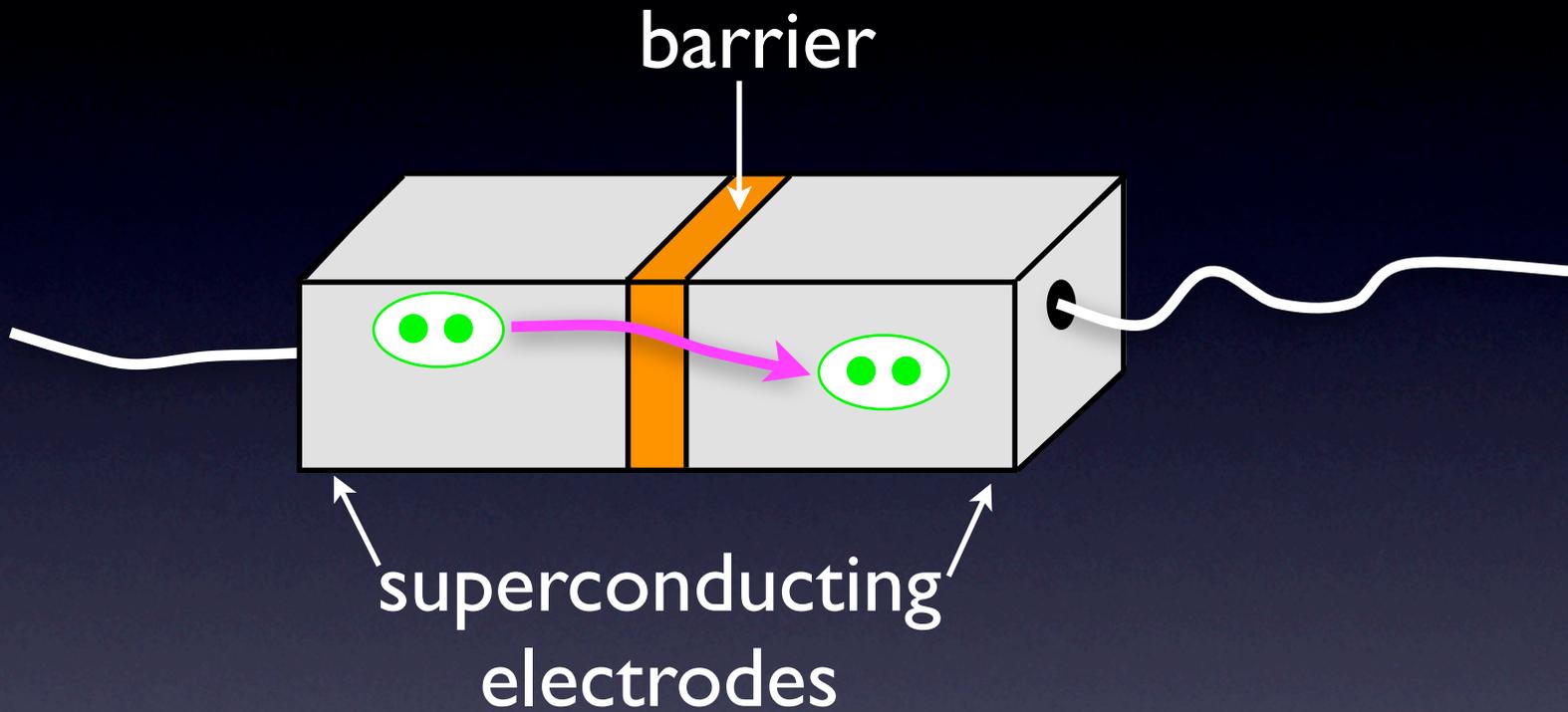
Quantum Computing

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The single pair box utilizes a Josephson junction between two superconducting electrodes. Pairs can tunnel coherently through such junctions. This may serve as a qubit.

High T_c Superconductors

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Nuclear electric power plants in remote areas.

Hydrogen economy.

Some of these applications we could foresee
but most we could not.

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In doing fundamental science, perhaps, most
important is what we cannot foresee.

Almost all of the technology we rely on for civilian and military use:

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Communications

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Computers

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In addition....

It is almost impossible to predict what technologies will flow from fundamental science.

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Maxwell, Lorentz, Einstein
(Electromagnetic Theory)

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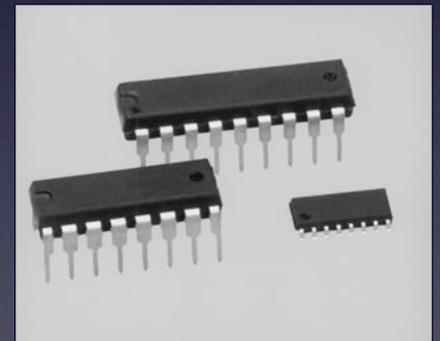
Mine detonator

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Schrödinger, Heisenberg
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Bloch, Purcell
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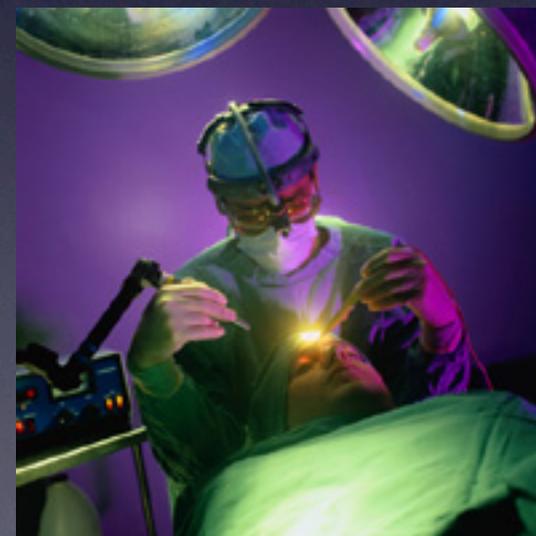
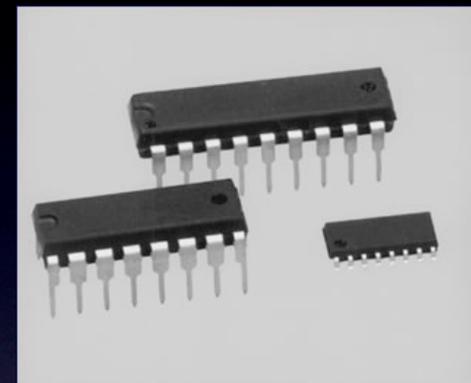
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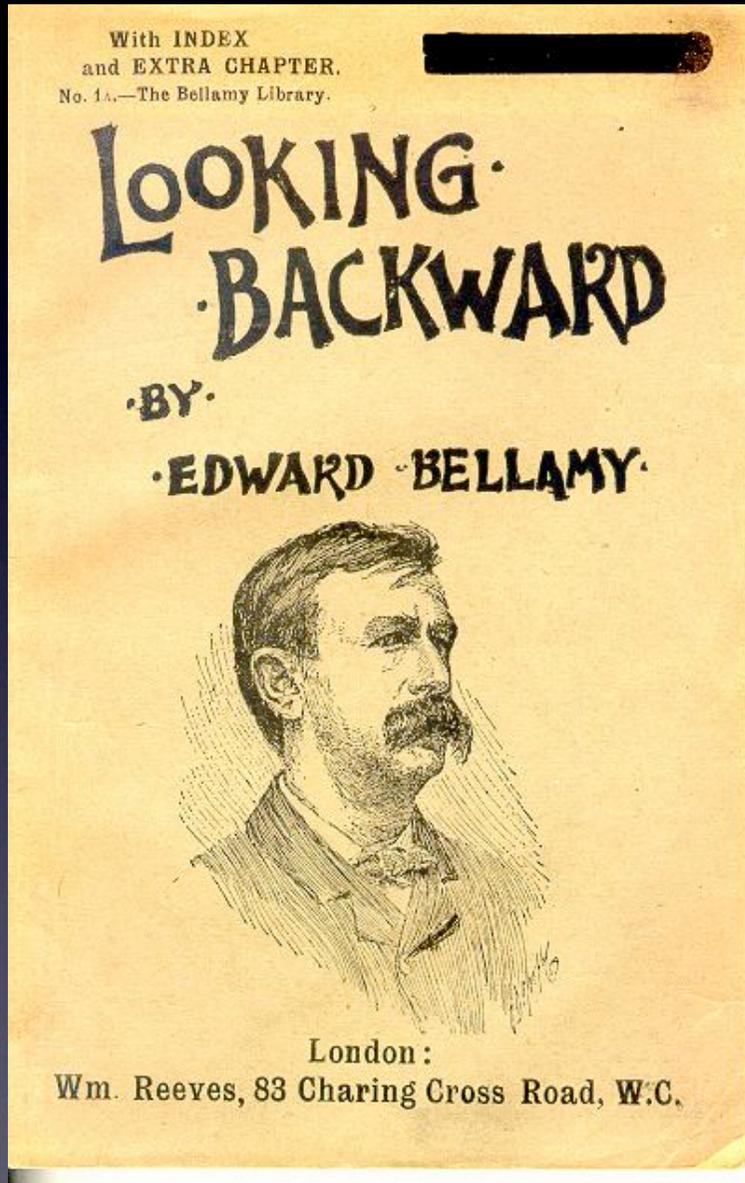
MRI

Premature targeted programs to obtain these technologies would have failed. Worse, resources would have been taken away from the scientists who in fact made them possible.

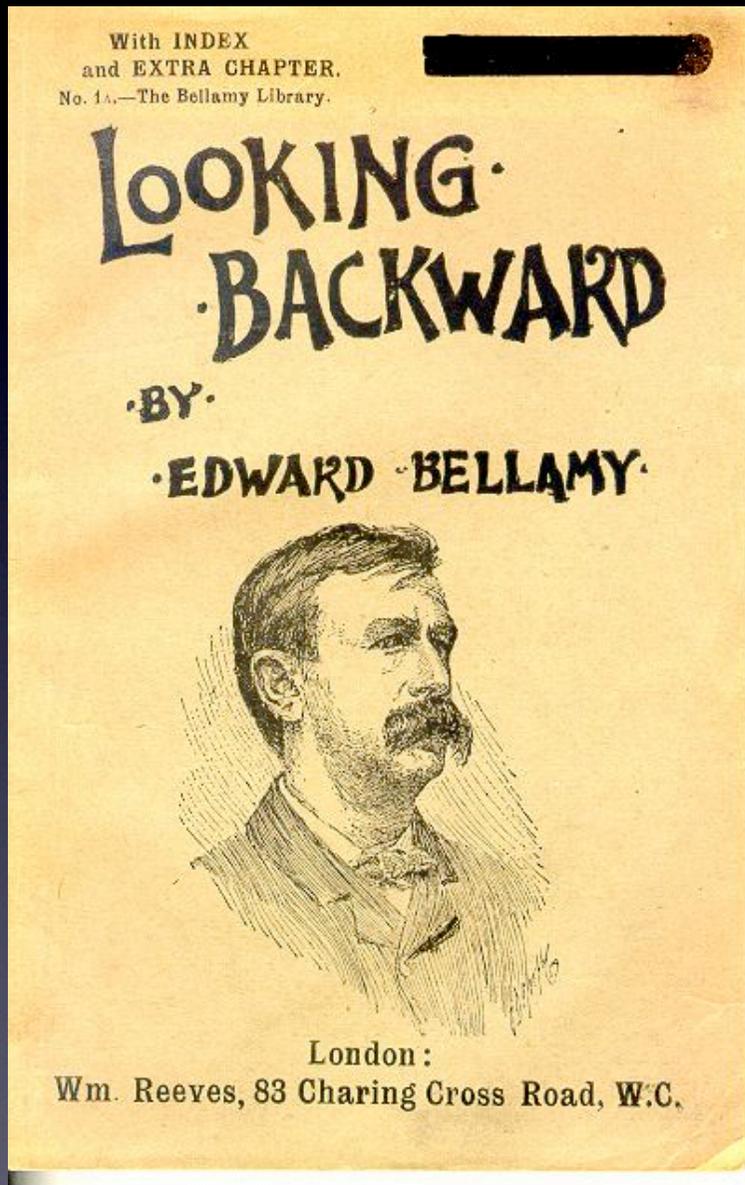
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In 1887 Edward Bellamy wrote, with a certain optimism:

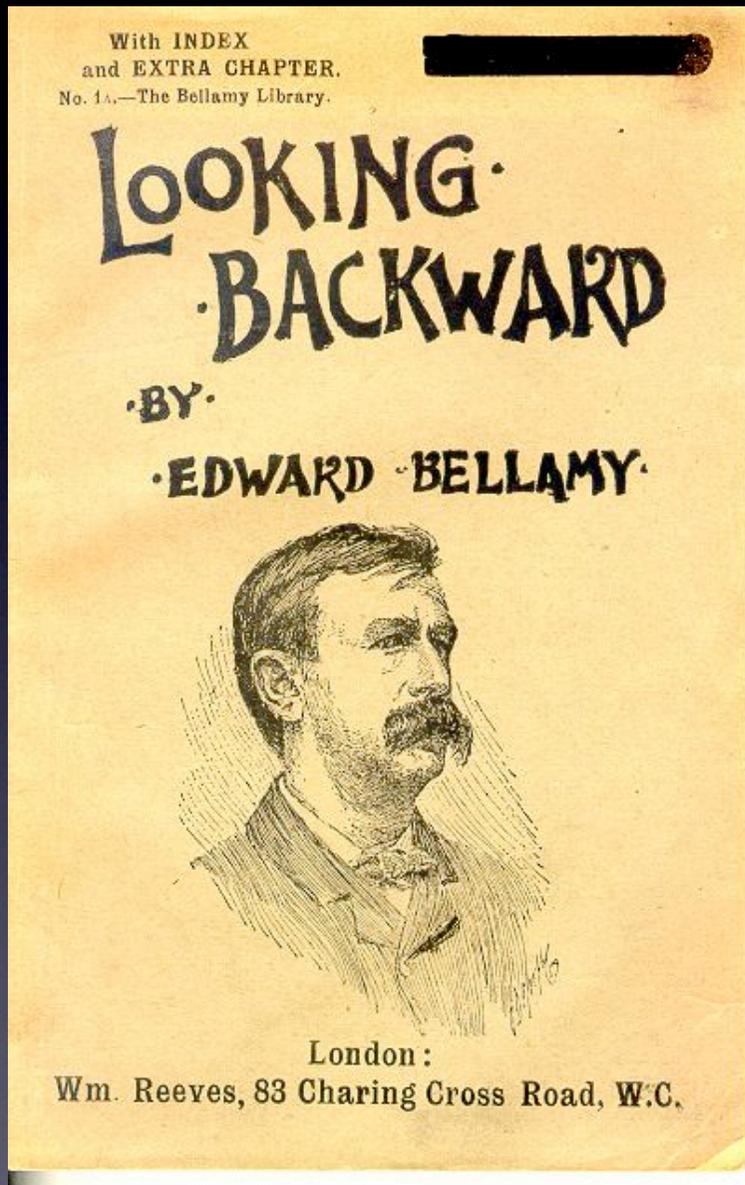


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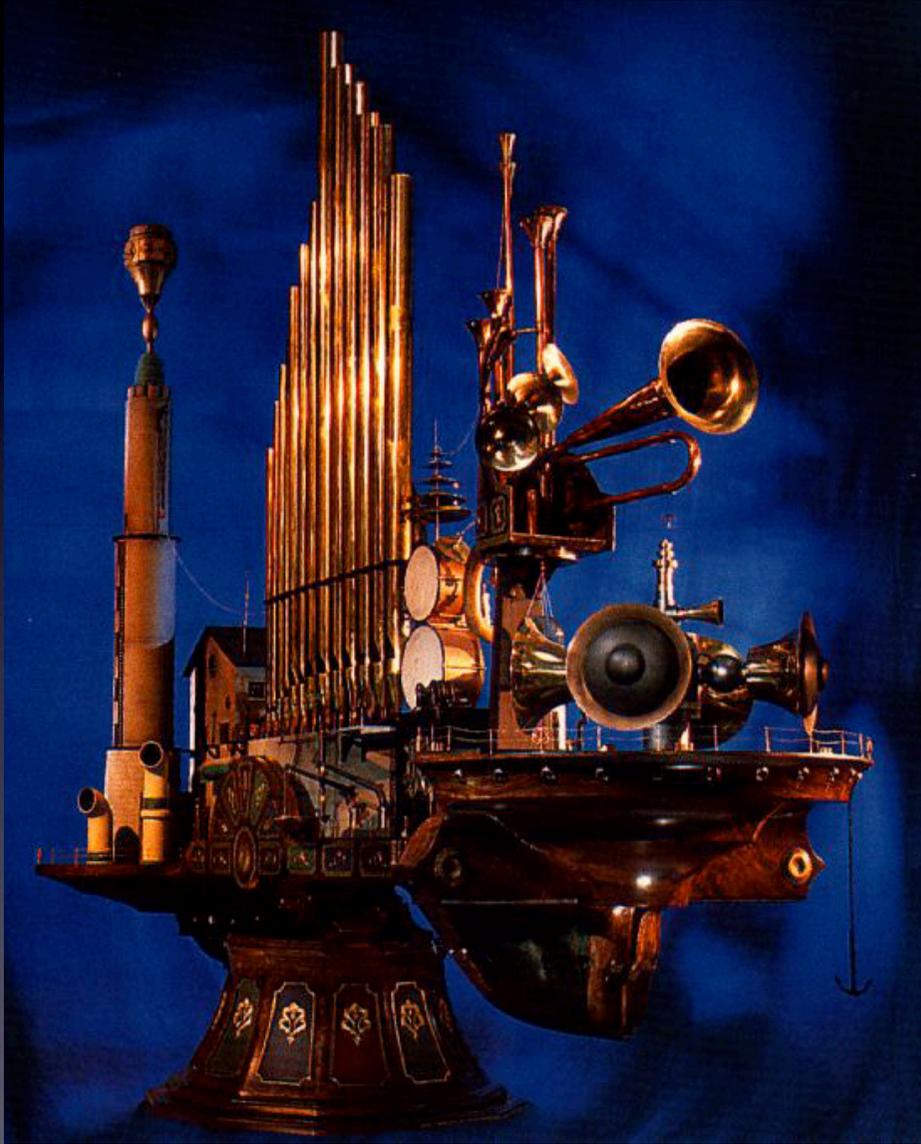


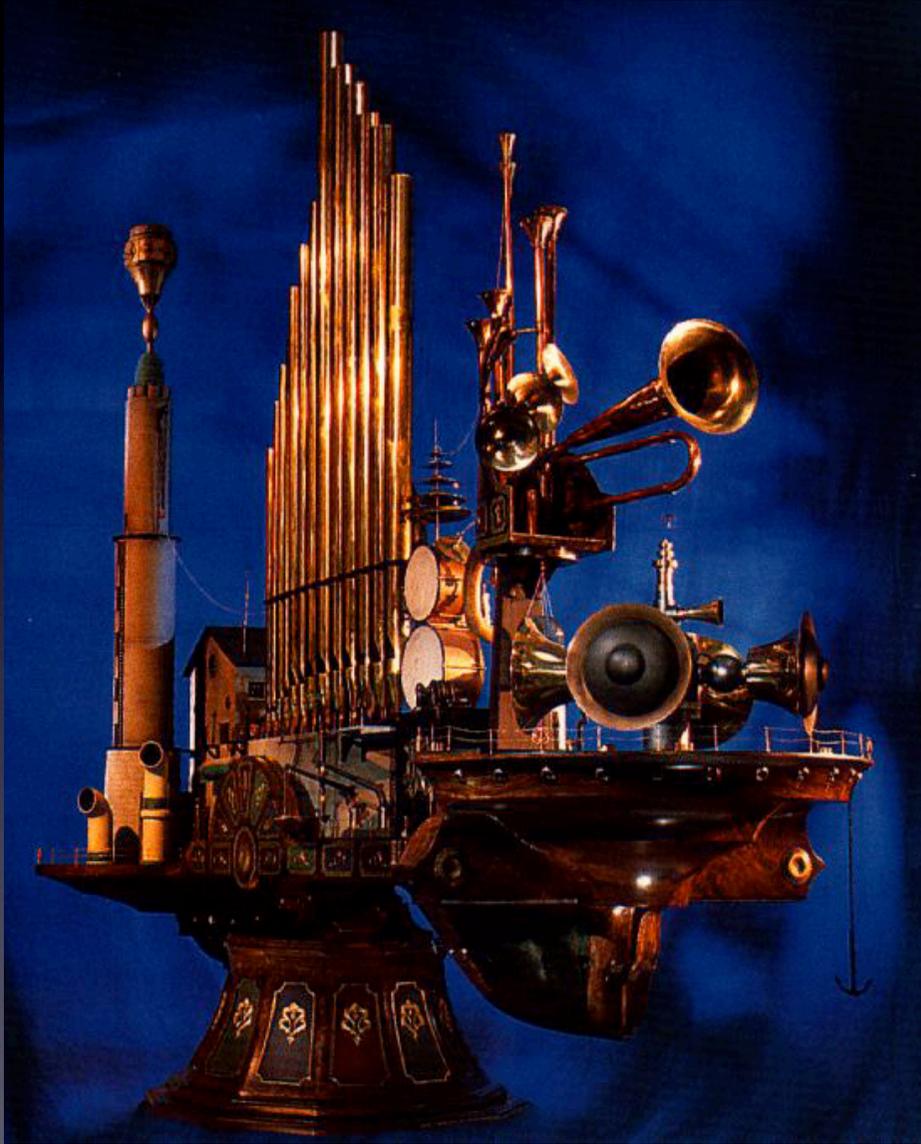
If we could have devised an arrangement for providing everybody with music in their homes, perfect in quality, unlimited in quantity, suited to every mood, and beginning and ceasing at will,

In 1887 Edward Bellamy wrote, with a certain optimism:



If we could have devised an arrangement for providing everybody with music in their homes, perfect in quality, unlimited in quantity, suited to every mood, and beginning and ceasing at will, we should have considered the limit of human felicity already attained, and ceased to strive for further improvements.





Theory of Superconductivity*

J. BARDEEN, L. N. COOPER,† AND J. R. SCHRIEFFER‡

Department of Physics, University of Illinois, Urbana, Illinois

(Received July 8, 1957)

A theory of superconductivity is presented, based on the fact that the interaction between electrons resulting from virtual exchange of phonons is attractive when the energy difference between the electrons states involved is less than the phonon energy, $\hbar\omega$. It is favorable to form a superconducting phase when this attractive interaction dominates the repulsive screened Coulomb interaction. The normal phase is described by the Bloch individual-particle model. The ground state of a superconductor, formed from a linear combination of normal state configurations in which electrons are virtually excited in pairs of opposite spin and momentum, is lower in energy than the normal state by amount proportional to an average $(\hbar\omega)^2$, consistent with the isotope effect. A mutually orthogonal set of excited states in

one-to-one correspondence with those of the normal phase is obtained by specifying occupation of certain Bloch states and by using the rest to form a linear combination of virtual pair configurations. The theory yields a second-order phase transition and a Meissner effect in the form suggested by Pippard. Calculated values of specific heats and penetration depths and their temperature variation are in good agreement with experiment. There is an energy gap for individual-particle excitations which decreases from about $3.5kT_c$ at $T=0^\circ\text{K}$ to zero at T_c . Tables of matrix elements of single-particle operators between the excited-state superconducting wave functions, useful for perturbation expansions and calculations of transition probabilities, are given.

I. INTRODUCTION

THE main facts which a theory of superconductivity must explain are (1) a second-order phase transition at the critical temperature, T_c , (2) an electronic specific heat varying as $\exp(-T_0/T)$ near $T=0^\circ\text{K}$ and other evidence for an energy gap for individual particle-like excitations, (3) the Meissner-Ochsenfeld effect ($\mathbf{B}=0$), (4) effects associated with infinite conductivity ($\mathbf{E}=0$), and (5) the dependence of T_c on isotopic mass, $T_c\sqrt{M}=\text{const}$. We present here a theory which accounts for all of these, and in addition gives good quantitative agreement for specific heats and penetration depths and their variation with temperature when evaluated from experimentally determined parameters of the theory.

When superconductivity was discovered by Onnes¹ (1911), and for many years afterwards, it was thought to consist simply of a vanishing of all electrical resistance below the transition temperature. A major advance was the discovery of the Meissner effect² (1933), which showed that a superconductor is a perfect diamagnet; magnetic flux is excluded from all but a thin penetration region near the surface. Not very long afterwards (1935), London and London³ proposed a phenomenological theory of the electromagnetic properties in which the diamagnetic aspects were assumed

basic. F. London⁴ suggested a quantum-theoretic approach to a theory in which it was assumed that there is somehow a coherence or rigidity in the superconducting state such that the wave functions are not modified very much when a magnetic field is applied. The concept of coherence has been emphasized by Pippard,⁵ who, on the basis of experiments on penetration phenomena, proposed a nonlocal modification of the London equations in which a coherence distance, ξ_0 , is introduced. One of the authors^{6,7} pointed out that an energy-gap model would most likely lead to the Pippard version, and we have found this to be true of the present theory. Our theory of the diamagnetic aspects thus follows along the general lines suggested by London and by Pippard.⁷

The Sommerfeld-Bloch individual-particle model (1928) gives a fairly good description of normal metals, but fails to account for superconductivity. In this theory, it is assumed that in first approximation one may neglect correlations between the positions of the electrons and assume that each electron moves independently in some sort of self-consistent field determined by the other conduction electrons and the ions. Wave functions of the metal as a whole are designated by occupation of Bloch individual-particle states of energy $\epsilon(\mathbf{k})$ defined by wave vector \mathbf{k} and spin σ ; in the ground state all levels with energies below the Fermi energy, ϵ_F , are occupied; those above are unoccupied. Left out of the Bloch model are correlations between electrons brought about by Coulomb forces and interactions between electrons and lattice vibrations (or phonons).

* This work was supported in part by the Office of Ordnance Research, U. S. Army. One of the authors (J. R. Schrieffer) was aided by a Fellowship from the Corning Glass Works Foundation. Parts of the paper are based on a thesis submitted by Dr. Schrieffer in partial fulfillment of the requirements for a Ph.D. degree in Physics, University of Illinois, 1957.

† Present address: Department of Physics and Astronomy, The Ohio State University, Columbus, Ohio.

‡ Present address: Department of Theoretical Physics, University of Birmingham, Birmingham, England.

¹ H. K. Onnes, *Comm. Phys. Lab. Univ. Leiden*, Nos. 119, 120, 122 (1911).

² W. Meissner and R. Ochsenfeld, *Naturwiss.* 21, 787 (1933).

³ H. London and F. London, *Proc. Roy. Soc. (London)* A149, 71 (1935); *Physica* 2, 341 (1935).

⁴ F. London, *Proc. Roy. Soc. (London)* A152, 24 (1935); *Phys. Rev.* 74, 562 (1948).

⁵ A. B. Pippard, *Proc. Roy. Soc. (London)* A216, 547 (1953).

⁶ J. Bardeen, *Phys. Rev.* 97, 1724 (1955).

⁷ For a recent review of the theory of superconductivity, which includes a discussion of the diamagnetic properties, see J. Bardeen, *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1956), Vol. 15, p. 274.

* This work was supported in part by the Office of Ordnance Research, U. S. Army.