Lecture 26 Highlights
Phys 402

The theory of superconductivity, formulated by Bardeen, Cooper and Schrieffer (BCS), is based on the concept of Cooper pairing of two electrons. Pairs of electrons will have a net spin of either 0 or 1, making them Bosonic in character. As such, they may then undergo Bose-Einstein condensation in to the ground state and show a "superfluid" phase similar to that of ^{4}He (this is not what happens, but it is good motivation for studying pairing). The Cooper pair calculation for two electrons added to a filled Fermi sea at zero temperature proceeds as follows. We ask the question: will there be a bound state of two electrons added to the filled Fermi sea if there is a weak attractive interaction between them? In other words, will the 2 electrons added to states at the Fermi Energy (E_F) have an eigenenergy that is less than $2E_F$?

We seek a solution to the 2-identical electron (Fermion) Schrödinger equation:

$$\left\{-\frac{\hbar^2}{2m}\nabla_1^2-\frac{\hbar^2}{2m}\nabla_2^2+V(\vec{r}_1,\vec{r}_2)\right\}\Psi(1,2)=E\Psi(1,2)\,, \qquad (1)$$

for the eigenenergy E. The 2-particle wavefunction for two identical Fermions must be overall anti-symmetric, or in other words: $\Psi(2,1)=-\Psi(1,2)$. We treat the two electrons as if they are "free" but confined to a box, with periodic boundary conditions. This gives rise to single-particle solutions of the form $\exp\left[\pm i\vec{k}\bullet\vec{r}\right]|\frac{1}{2}\ m_s\rangle$, which are "running wave" solutions of a spin-1/2 particle. If we add two particles to the filled Fermi sea (which means that all states of energy less than E_F are occupied, then the minimum center-of-mass energy would have the two electrons in states of equal and opposite momentum: $\Psi(1,2)\propto\exp\left[+i\vec{k}\bullet\vec{r}_1\right]\exp\left[-i\vec{k}\bullet\vec{r}_2\right]$, and $|\vec{k}|\geq k_F$, where k_F is the Fermi k-vector, defined as $E_F=\hbar^2k_F^2/2m$.

We assume the wavefunction can be written as a product of a space part and a spin part. Each can be either symmetric or anti-symmetric upon exchange of the coordinates of the two particles. Overall anti-symmetry of the wavefunction requires that one be symmetric and the other be anti-symmetric. To construct the full wavefunction there are just two possibilities:

$$\Psi_{SA}(1,2)=\cos\left(\vec{k}\bullet\vec{r}\right)|00\rangle$$

$$\Psi_{AS}(1,2)=\sin\left(\vec{k}\bullet\vec{r}\right)\begin{cases}|11\rangle\\|10\rangle\\|1-1\rangle\end{cases},$$

where $\vec{r}=\vec{r}_1-\vec{r}_2$ is the relative coordinate. If there is a small attractive interaction between the electrons, then the symmetric space wavefunction ($\Psi_{SA}(1,2)$) will be favored. This wavefunction puts the two electrons into a spin singlet state. The general wavefunction for the two electrons allows them to occupy any pair of states ($\vec{k},-\vec{k}$) outside the Fermi sphere:

$$\Psi(1,2)=\sum_{k>k_F}g_k\cos\left(\vec{k}\bullet\vec{r}\right)|00\rangle\,,$$

where g_k is a weighting function that depends only on the magnitude of $\vec{k}$ and not its direction (assuming the metal is isotropic), and the sum is over all momentum eigenstates outside the Fermi sphere.

Putting this *ansatz* into the Schrödinger equation (1) leads, after some manipulations (including sum busting) to:

$$(E - 2\varepsilon_k)g_k = \sum_{k'} g_{k'} V_{k,k'},$$

where $\varepsilon_k = \hbar^2 k^2 / 2m$ is the single-particle kinetic energy and $V_{k,k'} \equiv \int d^3 r\, V(r) \exp\left[i\left(\vec{k} - \vec{k}'\right) \bullet \vec{r}\right]$ is the Fourier transform of the pairing potential from real space into momentum space. We take the Cooper approximation for the attractive interaction between the electrons in momentum space. Fröhlich showed that two electrons can attract each other through a well-timed interaction with the vibrations of the positive ion crystal lattice. This attraction is retarded in time and is said to be mediated by the lattice. The approximate attractive potential is modeled as:

$$V_{k,k'} = \begin{cases} -V \text{ when } E_F \le \varepsilon_k \le E_F + \hbar\omega_c, \text{where } V > 0 \\ 0 \text{ when } \varepsilon_k > E_F + \hbar\omega_c \end{cases}$$

This potential favors pairing which involves scattering from states ($\vec{k}$,$-\vec{k}$) to states ($\vec{k}'$,$-\vec{k}'$) both of which are within a thin skin of thickness $\hbar\omega_c$ of the Fermi energy. The energy scale $\hbar\omega_c$ is the characteristic energy of the lattice vibrations (the Debye energy), and will depend on the material. However, it should be noted that $\hbar\omega_c \ll E_F$. Note that V is the depth of the attractive interaction well, and NOT the volume of the metal!

With this simplification of the potential one can solve for the eigenenergy of the two-electron problem;

$$E \cong 2E_F - 2\hbar\omega_c e^{-2/(N(E_F)V)},$$

where we have made the "weak coupling" approximation that $N(E_F)V << 1$, where $N(E_F)$ is the density of electronic states at the Fermi energy. This result shows that there is a bound state of the electrons for arbitrarily weak pairing interaction V. The resulting bound state is called a Cooper pair. Note that the binding energy is proportional to the lattice vibration energy ($\hbar\omega_c$), characterized by the Debye temperature Θ_D. In turn, this energy depends on the ion mass M as $\Theta_D \sim 1/\sqrt{M}$ (think of the harmonic oscillation of the ions in the inter-atomic potential well). Hence this calculation predicts that the transition temperature of the superconductor (proportional to the binding energy of the Cooper pair) will scale as $T_c \sim 1/\sqrt{M}$, or in other words $T_c\sqrt{M} = \text{constant}$. Experiments have been done with metals made up of different isotopes (which have different M), and this relationship is found to be basically correct. This is called the "isotope effect" and constitutes a significant success of the theory. This result also predicts that metals that have ions with small mass will have the highest transition temperatures. Indeed there is a recently discovered hydride material that has a T_c just below room temperature. Unfortunately, this material is only stable at extremely high pressures!

Another thing to note about the solution for the two-electron energy, $E \cong 2E_F - 2\hbar\omega_c e^{-2/(N(E_F)V)}$, is that it cannot be expanded in a convergent power series in the small parameter ($N(E_F)V << 1$). Note that the series expansion for the exponential is

actually in inverse powers of the small parameter! This is why many physicists like Einstein and Feynman failed to explain superconductivity by means of perturbation theory. This result is said to be a "non-perturbative solution," and represents a whole new class of solutions to the Schrodinger equation.

The full BCS theory of superconductivity builds the Cooper pairing into the wavefunction for all the electrons in the metal, not just these two "special case" electrons. The BCS ground state wavefunction is a statistical occupation of paired and un-paired states that promotes a certain fraction of the electrons outside the Fermi sea to take advantage of the attractive pairing interaction (which is only active for $k > k_F$). That result earned them a Nobel prize in physics (the second for Bardeen), and their theory has had a profound influence on theoretical physics since then.