Relativistic mass corrections for rotating superconductors

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The relativistic Hamiltonian and Dirac current density for a charged particle in a rotating frame are derived. Simple results are obtained correct to all orders in the particle velocity and to first order in the rotation velocity. An extension is made to the many-electron current and is used for calculating the relativistic corrections to the magnetic field generated within a rotating superconductor (London moment). With the use of simple solid-state models, estimates of the corrections for common elemental superconductors are presented. The results predict several hundred ppm corrections for most superconductors and are of direct significance to high-precision measurements of h/m_e now under way at Stanford. In addition, comparison of the experimental values with the accepted value of h/m_e for the free electron at rest will provide a direct measure of the expectation value for the kinetic energy of the electron wave functions averaged over the Fermi surface, a quantity not observed directly by any other technique.

I. INTRODUCTION

The first successful measurements of the mass-to-charge ratio of the electron using accelerated conductors were performed by Tolman[1] and co-workers in the 1910s and 1920s on oscillating normal metallic cylinders. These clearly demonstrated that electrons are the current carriers in metals. In 1933 Becker[2] and co-workers first predicted that a resistanceless conductor rotated from rest would exhibit a magnetic moment proportional to its spin speed. The effect came to be known as the London moment after the phenomenological theory of F. London and H. London[3] was applied by F. London[4] to a rotating superconductor. He predicted a uniform magnetic field

$$\vec{B}_L = -\frac{2mc}{e}\vec{\omega} \tag{1}$$

within the rotating superconducting lattice. It was first observed by Hildebrandt[5] and has been verified many times to an accuracy approaching a few percent.[6–10]

Beginning in 1967 and continuing into the 1970s, high-precision measurements of $h/2e$ have been based on the ac Josephson effect.[11–13] A resolution better than 0.1 parts per million (ppm) has been achieved, which is by far the most accurate determination of any property of a solid-state system. At that time several suggestions were made for measurements of h/m in rotating superconducting rings,[14] again taking advantage of the unique properties of the macroscopic quantum nature of the superconducting state. These are based on balancing the magnetic flux from an integral number of flux quanta $n(hc/2e)$ against the London moment flux $(2mc/e)\omega S$, where S is the cross-section area of the ring. Several experiments have measured h/m in this way,[15,16] with the most accurate result reported by Parker and Simmonds[16] in 1970 at a resolution of 400 ppm. It is in agreement with the accepted value for the free electron at rest obtained by other techniques. As Josephson[17] pointed out, the arguments for the derivation of equations containing h/m have been based on Galilean invariance rather than Lorentz invariance. Two possible sources for relativistic corrections have been mentioned: the relativistic mass shift due to the Fermi velocity[16,17] and surface effects characterized by the metallic work function.[17]

Technological advances in magnetic shielding,[18] superconducting quantum interference device (SQUID) magnetometry,[19] cryogenic rotors,[20] and high-precision dimensional metrology[21] during the past decade, primarily associated with the relativity gyroscope experiment,[20] now allow a significant improvement in these measurements. With experimental work now underway at Stanford to perform measurements on rotating superconducting rings at a resolution approaching 1 ppm, we felt a thorough theoretical examination of these relativistic corrections to be necessary.

In this paper we present a formalism for calculating the relativistic corrections involved in measurements of h/m using rotating superconducting rings. It is shown that the mass-velocity correction for the conduction electrons on the Fermi surface dominates all other effects, usually by an order of magnitude. However, it is *not* the Fermi velocity but the expectation value of the kinetic energy which enters into the final expression. The portions of the electron wave functions near the atomic cores dominate this expectation value. Our estimates predict several hundred ppm corrections for many superconductors.

Outlining our approach, in Sec. II we give a brief summary of the nonrelativistic treatment of the rotating superconductor. In Sec. III the relativistic Hamiltonian for a charged particle in a rotating frame is derived. A simple result is obtained correct to all orders in the particle velocity and to first order in the rotational velocity. Motivated by this result, in Sec. IV we derive the Dirac current density in a rotating frame, again to first order in the rotational velocity, but otherwise exact. An extension to the relativistic many-body electron current is made in Sec. V and used in Sec. VI, where we derive the form of the relativistic corrections to the London moment and make estimates for various elemental superconductors using simple solid-state models. In Sec. VII we complete the derivation of the theory for the rotating-ring experiment to measure h/m and include discussions of other smaller corrections.

II. THE LONDON MOMENT

The London moment in a rotating superconductor results from the Coriolis force on a charged particle in a rotating frame of reference.[22] This force is derived from a vector potential which appears in the Hamiltonian of a particle in the rotating frame on an equal footing with the ordinary electromagnetic vector potential. In the nonrelativistic limit this Hamiltonian is[23]

$$H=\frac{1}{2m}\left[\vec{p}-\frac{e}{c}[\vec{A}(\vec{r})+\vec{A}_\omega(\vec{r})]\right]^2 -\tfrac{1}{2}m(\vec{\omega}\times\vec{r})^2+e\Phi(\vec{r}) \,, \qquad (2)$$

where $-e$ is the charge of the electron,

$$\vec{A}_\omega(\vec{r})=\frac{mc}{e}(\vec{\omega}\times\vec{r}) \,, \qquad (3)$$

and $\vec{\omega}$ is the angular velocity of the rotation. The second term represents the centrifugal potential which gives rise to a radial electric field balancing the centrifugal force induced by the rotation, and the last term is the potential energy of the particle in the scalar potential $\Phi(\vec{r})$. The electrodynamics of a superconductor is described by Maxwell's equations together with London's phenomenological equation for the supercurrent,[4]

$$\vec{j}=-\frac{n_s e^2}{mc}\vec{A} \,. \qquad (4)$$

The electromagnetic properties of a rotating superconductor are the same as those of a stationary superconductor but with $\vec{A}$ replaced by the effective vector potential $\vec{A}+\vec{A}_\omega$. In the case of simply connected bodies the Meissner effect implies

$$\vec{B}+\vec{B}_\omega=0 \,, \qquad (5)$$

which means that the rotation gives rise to a magnetic field

$$\vec{B}_L=-\vec{\nabla}\times\vec{A}_\omega=-\frac{2mc}{e}\vec{\omega} \,. \qquad (6)$$

In the case of thick multiply connected bodies, the rotation modifies the flux quantization constraint

$$\oint(\vec{A}+\vec{A}_\omega)\cdot d\vec{l}=n\frac{hc}{2e} \,. \qquad (7)$$

This equation forms the basis for the experimental measurements described in Sec. VII.

One should mention at this point that the electron mass in Eq. (6) is the bare mass and not the effective mass which appears in the dynamic and thermodynamic properties of electrons in the solid. The easiest way to see this is by starting from the full Hamiltonian of the solid including the electrons, the ions, and all their interactions. Transforming to the rotating frame, one finds again that each electron "feels" the additional effective vector potential given in Eq. (3), regardless of its complicated interaction with the ions and the other electrons.

III. THE RELATIVISTIC HAMILTONIAN

To obtain the relativistic expression for the Coriolis vector potential $\vec{A}_\omega$ we have to start from the relativistic Hamiltonian. The Hamiltonian of a charged particle in a general noninertial frame of reference, characterized by the metric tensor $g_{\mu\nu}$, was derived by DeWitt[24] and Papini,[25]

$$H=c(g^{ij}g_{0i}g_{0j}-g_{00})^{1/2}(m^2c^2-g^{kl}\pi_k\pi_l)^{1/2} -cg^{ij}g_{0j}\pi_i+eA_0 \,, \qquad (8)$$

where $\pi_k=p_k-(e/c)A_k$, A_0 is the scalar potential

$\Phi(\vec{r})$, and summation over repeated indices is implied. The metric tensor $g_{\mu\nu}$ in the case of a uniform rotation with angular velocity $\vec{\omega}$ is given by[26]

$$\begin{aligned} g_{00}&=-1+\frac{1}{c^2}(\vec{\omega}\times\vec{r})^2\ ,\\ g_{kk}&=1\ ,\\ g_{k0}&=g_{0k}=\frac{1}{c}(\vec{\omega}\times\vec{r})_k\ . \end{aligned} \tag{9}$$

The inverse metric tensor $g^{\mu\nu}$ is

$$\begin{aligned} g^{00}&=-1\ ,\\ g^{kk}&=1-\frac{1}{c^2}(\vec{\omega}\times\vec{r})_k^2\ ,\\ g^{0k}&=g^{k0}=\frac{1}{c}(\vec{\omega}\times\vec{r})_k\ ,\\ g^{kl}&=g^{lk}\\ &=-\frac{1}{c^2}(\vec{\omega}\times\vec{r})_k(\vec{\omega}\times\vec{r})_l \quad \text{for } k\neq l\ . \end{aligned} \tag{10}$$

Inserting (9) and (10) into Eq. (8), one gets

$$\begin{aligned} H=&\left[1-\frac{(\vec{\omega}\times\vec{r})^4}{c^4}\right]^{1/2}\\ &\times[m^2c^4+c^2\pi^2-(\vec{\omega}\times\vec{r})_k(\vec{\omega}\times\vec{r})_l\pi_k\pi_l]^{1/2}\\ &-\left[1-\frac{(\vec{\omega}\times\vec{r})^2}{c^2}\right](\vec{\omega}\times\vec{r})_l\pi_l+e\Phi\ . \end{aligned} \tag{11}$$

We shall now neglect terms of order $(\omega r/c)^2$. In the experiment under consideration this amounts to an error of order 10^{-14}, far below the experimental accuracy. This leaves us with a Hamiltonian which treats the particle velocity relativistically and the rotational velocity classically,

$$\begin{aligned} H=&\left[m^2c^4+c^2\left[\vec{p}-\frac{e}{c}\vec{A}\right]^2\right]^{1/2}\\ &-\left[\vec{p}-\frac{e}{c}\vec{A}\right]\cdot(\vec{\omega}\times\vec{r})+e\Phi\ . \end{aligned} \tag{12}$$

The nonrelativistic limit of this expression is the Hamiltonian in Eq. (2). It is worth pointing out that Eq. (12) can be obtained in the classical way from the Lagrangian of a charged particle,

$$L=-mc^2\left[1-\frac{v^2}{c^2}\right]^{1/2}+\vec{A}\cdot\vec{v}-e\Phi\ , \tag{13}$$

by replacing $\vec{v}=\vec{v}+\vec{\omega}\times\vec{r}$ in the first term only. This procedure approximates the transformation to the noninertial rotating frame by a local Galilean transformation at each point $\vec{r}$. The last two terms on the right-hand side of Eq. (13) form a world scalar and are unaffected by such a transformation.

Returning to Eq. (12), we want to express it in the form

$$H'=\left\{m^2c^4+c^2\left[\vec{p}-\frac{e}{c}\left[\vec{A}+\alpha\frac{mc}{e}(\vec{\omega}\times\vec{r})\right]\right]^2\right\}^{1/2}+e\Phi\ , \tag{14}$$

choosing α so that H' will be identical to H in Eq. (12) to lowest order in $\omega r/c$. Comparing the first derivatives of Eqs. (12) and (14) with respect to $(\vec{\omega}\times\vec{r})$, one finds

$$\alpha=\frac{1}{mc^2}(m^2c^4+c^2\pi^2)^{1/2}=\frac{E-e\Phi}{mc^2}=\gamma\ , \tag{15}$$

where γmc^2 is the relativistic kinetic energy and E is the total relativistic energy. Note that γ reduces to the familiar form $[1-(v^2/c^2)]^{-1/2}$ for a free electron. Thus, the Coriolis vector potential of a relativistic particle is, up to the first order in the rotational velocity, given by

$$\vec{A}_\omega=\gamma\frac{mc}{e}(\vec{\omega}\times\vec{r})\ . \tag{16}$$

We have shown that relativistically the effect of rotation retains its equivalence to the presence of a magnetic field. This is not a trivial conclusion and is strictly true only for nonrelativistic rotation velocities. The application of a magnetic field to a system adds to the Hamiltonian a term involving the current, whereas a uniform rotation involves the momentum. However, as in nonrelativistic theory, the two can still be equated provided the relativistic mass shift is included. Thus we may write

$$\vec{p}=\gamma m\vec{v}=\frac{\gamma m}{e}\vec{j}\ ,$$

because of the isotropic nature of the relativistic mass shift. The proportionality constant is no longer independent of the particle dynamics as it was in the nonrelativistic case; however, as we show below, it carries interesting information on the particle dynamics.

IV. THE RELATIVISTIC SINGLE-ELECTRON CURRENT

We shall now derive the same result in a different way, which will allow us to make direct contact with quantum mechanics. This is not necessary for the discussion of the London moment itself, because quantum mechanics play no explicit role in London's original derivation, once the phenomenological equation (4) is postulated. However, we shall ultimately have to calculate the relativistic mass shift of an electron in the solid, and this can be done only in the framework of quantum mechanics.

We start from the Dirac relativistic expression for the current vector[27]

$$\vec{j} = ec\psi^\dagger \vec{\alpha}\psi \ , \tag{17}$$

where ψ is the Dirac 4-spinor, and the 4×4 matrices α_k are

$$\alpha_k = \begin{bmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{bmatrix} , \tag{18}$$

where σ_k are the Pauli spin matrices. The components of j are the spatial components of the current 4-vector j_μ, which transforms under a Lorentz transformation as the 4-vector x_μ. We shall transform $\vec{j}$ to a rotating frame of reference by performing at each point a transformation to a coordinate system moving with velocity $\vec{v}(\vec{r}) = \vec{\omega}\times\vec{r}$ and taking the Galilean limit of this transformation. The discussion of Eq. (12) justifies this procedure, showing that the resulting error is of order $(\omega r/c)^2$. The result of this transformation is

$$\vec{j} = ec\psi^\dagger\vec{\alpha}\psi - e(\vec{\omega}\times\vec{r})\psi^\dagger\psi \ . \tag{19}$$

The spinor ψ consists of two "large" and two "small" components. Let us rewrite Eq. (19) in terms of these components:

$$\vec{j} = ec(\psi_L^\dagger\vec{\sigma}\psi_s + \psi_s^\dagger\vec{\sigma}\psi_L) - e(\vec{\omega}\times\vec{r})(\psi_L^\dagger\psi_L + \psi_s^\dagger\psi_s) \ , \tag{20}$$

where ψ_L, ψ_s are 2-spinors of the "large" and "small" components, respectively. We use the Dirac equation to express ψ_s in terms of ψ_L,[27]

$$\psi_s = \frac{c(\vec{\sigma}\cdot\vec{\pi})}{2mc^2 + E' - e\Phi}\psi_L \ , \tag{21}$$

where $E' = E - mc^2$, E being the total relativistic energy of the particle. Inserting Eq. (21) into Eq. (20) one obtains after tedious but straightforward manipulations

$$\vec{j} = \frac{ec^2}{(2mc^2+E'-e\Phi)}[\psi_L^\dagger\vec{\pi}\psi_L + (\vec{\pi}\psi_L)^\dagger\psi_L - \hbar\vec{\nabla}\times\psi_L^\dagger\vec{\sigma}\psi_L] - e(\vec{\omega}\times\vec{r})\left[\psi_L^\dagger\psi_L + \frac{c^2}{(2mc^2+E'-e\Phi)^2}\psi_L^\dagger\left[\vec{\pi}^2 - \frac{e\hbar}{c}\vec{\sigma}\cdot\vec{\nabla}\times\vec{A}\right]\psi_L\right] . \tag{22}$$

The last term in the first bracket is the spin current, which vanishes when the total current of a Cooper pair is considered. For the same reason, the term with $\vec{\sigma}\cdot\vec{\nabla}\times\vec{A}$ does not contribute in our case. The remaining terms can be combined together to give

$$\vec{j} = \frac{ec^2}{(2mc^2+E'-e\Phi)} \times \left[\psi_L^\dagger\left[\vec{p} - \frac{e}{c}(\vec{A}+\vec{A}_\omega)\right]\psi_L + \text{H.c.}\right] , \tag{23}$$

where

$$\vec{A}_\omega = \frac{mc}{e}\left[1 + \frac{E'-e\Phi}{2mc^2} + \frac{c^2\vec{\pi}^2}{2mc^2(2mc^2+E'-e\Phi)}\right] \times(\vec{\omega}\times\vec{r}) \ . \tag{24}$$

This expression is exact to first order in $\omega r/c$ and to all orders in v/c (where v is now the particle velocity). Using $E' = E - mc^2$ and $c^2\pi^2 = (E-e\Phi)^2 - m^2c^4$, one finds that the expression in large parentheses is identical with γ of Eq. (15).

For our purpose here, we shall now approximate Eq. (24), keeping terms to order $(v/c)^2$. We first neglect $E' - e\Phi$ in the denominator of the third term. Next we assume that E' is the nonrelativistic limit of $E - mc^2$; namely, it is the energy obtained from the Schrödinger equation. In this approximation, $E' - e\Phi$ is equal to the kinetic energy, and the second and third terms can be combined to give

$$\vec{A}_\omega = \frac{mc}{e}\left[1 + \frac{E'-e\Phi}{mc^2}\right](\vec{\omega}\times\vec{r}) \ . \tag{25}$$

Note that classically, the expression in the first parentheses is $1 + v^2/2c^2$, which is the value of γ to lowest order in $(v/c)^2$.

V. EXTENSION TO RELATIVISTIC MANY-ELECTRON CURRENT

Equation (23) represents the relativistic current density of a single electron in a rotating system, and Eq. (25) is the vector potential associated with the rotation, again, for a single electron. In generalizing to a many-electron system, like the conduction band in a metal, we must calculate the relativistic mass correction taking into account the many-body interactions in a solid. In addition, we have to keep in mind that the mass correction γ depends on the electron kinetic energy and is therefore not the same for all the electrons in the Fermi sea. In this section we show that the mass correction is given by an averaged value of γ over only Fermi-surface states. We argue that although each electron in the conduction band participates in the supercurrent, the contributions from all but a narrow band around the Fermi surface cancel out exactly.

First we consider the simpler case of free electrons in a one-dimensional ring. The ground-state energy is

$$E=\frac{L}{\pi\hbar}\int_{-p_F}^{p_F}dp\left\{\left[m^2c^4+c^2\left[p-\frac{e\phi}{cL}\right]^2\right]^{1/2}-\left[p-\frac{e\phi}{cL}\right](\vec{\omega}\times\vec{r})_\theta\right\}, \tag{26}$$

where L is the circumference of the ring, p_F is the Fermi momentum, ϕ is the flux through the ring which is related to the vector potential by $\phi=A_\theta L$, and the index θ is the tangential component of the vector. We have used two spin states per momentum state. The current at $T=0$ is given by[28]

$$I=c\frac{dE}{d\phi}\ . \tag{27}$$

Thus,

$$I=\frac{L}{\pi\hbar}\int_{-p_F}^{p_F}dp\left[\frac{-ec^2(p-Q)}{L\,[m^2c^4+c^2(p-Q)^2]^{1/2}}+\frac{e}{L}(\vec{\omega}\times\vec{r})_\theta\right], \tag{28}$$

where $Q=e\phi/cL$. It is instructive to rewrite this expression in the form

$$I=-\frac{ec^2}{\pi\hbar}\int_{p_F-Q}^{p_F+Q}\frac{p'dp'}{(m^2c^4+c^2p'^2)^{1/2}}+\frac{2e}{\pi\hbar}p_F(\vec{\omega}\times\vec{r})_\theta\ , \tag{29}$$

which is obtained from Eq. (28) by substituting $p'=p-Q$, and noting that the integrand is odd and therefore there is no contribution from the interval $[-p_F,p_F]$. Equation (29) shows that although all of the states are shifted by Q, the momentum states which contribute to the net current are restricted to states within Q of p_F. In general, $Q<<p_F$ and the current can be written, to a very good approximation, as

$$I=-A_\theta\frac{2ce^2p_F}{\pi\hbar}\frac{1}{(m^2c^4+c^2p_F^2)^{1/2}}+\frac{2ep_F}{\pi\hbar}(\vec{\omega}\times\vec{r})_\theta\ . \tag{30}$$

If we ask what vector potential must be applied to the rotating ring to obtain zero current, one finds the London moment

$$A_\omega=\frac{mc}{e}\gamma(p_F)(\vec{\omega}\times\vec{r})_\theta\ , \tag{31}$$

where $\gamma(p_F)$ is evaluated at the Fermi momentum.

To include interactions we note from Eq. (15) that only the kinetic-energy part of the total energy contributes to γ, so that the generalization of Eq. (31) becomes

$$A_\omega=\frac{mc}{e}\left[1+\frac{E'-\langle p_F\,|\,\Phi\,|\,p_F\rangle}{mc^2}\right](\vec{\omega}\times\vec{r})_\theta\ . \tag{32}$$

In a three-dimensional system the derivation of Eq. (30) requires integration over the Fermi surface, and thus the expectation value of the potential energy in Eq. (32) becomes an average over all Fermi-surface states. In a general lattice the cancellation within the Fermi sea remains exact as long as $\vec{p}$ and $-\vec{p}$ are time-reversed conjugate states.

To be more precise, we note that the energy interval around the Fermi energy which is involved in the London moment is determined by the vector potential as in Eq. (29) only when the occupation of the momentum states is given by $n(\vec{p})=1$ for $|\vec{p}|\le p_F$ and $n(\vec{p})=0$ for $|\vec{p}|>p_F$. In a superconductor this sharp momentum distribution is modified by the pairing interactions. The energy interval which contributes to the supercurrent can be found exactly in the limit $T\to T_c$. To this end, let us evaluate the gap function $\Delta(\vec{r})$ in this limit. Generally,[29]

$$\Delta(\vec{r})=V\sum_l v_l^*(\vec{r})u_l(\vec{r})[1-2f(E_l)]\ , \tag{33}$$

where $u_l(\vec{r})$ and $v_l(\vec{r})$ are the wave functions used in the Bogoliubov transformation, $f(E_l)$ is the Fermi-Dirac distribution at the quasiparticle energy E_l, and l labels the single-particle states. Considering a weak current, characterized by wave vector $\vec{q}$, we have

$$v_l(\vec{r})=v_l e^{i(\vec{l}-\vec{q})\cdot\vec{r}},$$
$$u_l(\vec{r})=u_l e^{i(\vec{l}+\vec{q})\cdot\vec{r}}, \quad (34)$$

where

$$\begin{bmatrix} v_l \\ u_l \end{bmatrix}=\left[\frac{1}{2}\left[1\mp\frac{\xi_l}{E_l}\right]\right]^{1/2} \quad (35)$$

and

$$E_l=(\xi_l^2+\Delta_l^2)^{1/2}-\frac{\hbar^2}{2m}\vec{l}\cdot\vec{q} \ . \quad (36)$$

ξ_l is the normal-state single-electron energy measured from the Fermi energy, and Δ_l is the gap parameter which depends on T. Substituting Eqs. (34) into (33), we find

$$\Delta(\vec{r})=Ve^{2i\vec{q}\cdot\vec{r}}\sum_l v_l u_l \tanh\left[\frac{E_l}{2kT}\right] . \quad (37)$$

In the limit $(\hbar^2/2m)\vec{l}\cdot\vec{q} \ll \Delta_l$ and $T\rightarrow T_c$: $u_l\rightarrow 1$, $v_l\rightarrow\Delta(T)/2\xi_l$, $E_l\rightarrow\xi_l$, so that

$$\Delta(\vec{r})=V\Delta(T)e^{i2\vec{q}\cdot\vec{r}}\sum_l\frac{\tanh(\xi_l/2kT_c)}{2\xi_l} . \quad (38)$$

The function in the summation is strongly peaked at $\xi_l=0$ with a half-width of nearly $4kT_c$ which is equal to the gap energy Δ at $T=0$. In this limit Gorkov[30] has shown the gap function $\Delta(\vec{r})$ to be exactly proportional to the Ginzburg-Landau order parameter $\psi(\vec{r})$. Since the supercurrent is given by the order parameter as

$$\vec{j}=\frac{e\hbar}{2im}(\psi^*\vec{\nabla}\psi-\psi\vec{\nabla}\psi^*)-\frac{2e^2\psi^*\psi}{mc}\vec{A} , \quad (39)$$

one concludes from Eq. (38) that the states contributing to the net supercurrent are restricted to an energy interval of order Δ around the Fermi energy. This is generally larger than the energy interval determined by Q in Eq. (29) but still very small compared to the Fermi energy itself, so an average of γ over the Fermi surface provides a good approximation to order Δ/ϵ_F (usually $10^{-3}-10^{-4}$).

VI. ESTIMATE OF THE RELATIVISTIC CORRECTION

From Sec. V, we now obtain an expression for the relativistic shift of the London moment by inserting Eq. (32) into Eq. (6). Thus

$$\left[\frac{\Delta B_L}{B_L}\right]_{\rm rel}=\left\langle\frac{E'-e\langle\Phi\rangle}{mc^2}\right\rangle_{\rm av}=\gamma-1 , \quad (40)$$

where $\langle\ \rangle_{\rm av}$ denotes an average over the Fermi surface. The second numerator in Eq. (40) is also the average kinetic energy of electrons on the Fermi surface, and we can equivalently write

$$\left[\frac{\Delta B_L}{B_L}\right]_{\rm rel}=\frac{\langle p^2\rangle_{\rm av}/2m}{mc^2}=\gamma-1 . \quad (41)$$

When the electrons in a metal are described reasonably well by a tight-binding approximation,

$$\psi_k(\vec{r})=\frac{1}{\sqrt{N}}\sum_i e^{i\vec{k}\cdot\vec{R}}\varphi(\vec{r}-\vec{R}_i) , \quad (42)$$

where φ is an atomic wave function centered at the lattice site $\vec{R}_i$, and the kinetic energy is given by its atomic expectation value. This is the case for the d electrons in the transition metals. In general, an electron in the solid is described by a Bloch function,

$$\psi_k(\vec{r})=u_k(\vec{r})e^{i\vec{k}\cdot\vec{r}} . \quad (43)$$

The expectation value of the kinetic energy may be written in this case as

$$\langle k_F\,|\,T\,|\,k_F\rangle_{\rm av}=\frac{\hbar^2}{2m}\langle k_F^2\rangle_{\rm av}+\frac{\hbar^2}{2m}\left\langle\int d^3r\,u_{k_F}^*(\vec{r})\nabla^2 u_{k_F}(\vec{r})\right\rangle_{\rm av} . \quad (44)$$

On the right-hand side we have dropped the cross term, which is proportional to $\vec{k}_F$ and therefore cancels out after averaging over the Fermi surface. The first term in (44) is the Fermi energy, and the second term is a core contribution which will now be smaller than in the atomic case, because the wave function is spread over a larger volume of the Wigner-Seitz cell.

We find that the dominant contribution to $\langle p^2\rangle$, or $\langle\Phi\rangle$, comes from the atomic cores. To get an estimate of the magnitude we have computed $\langle T\rangle$ for the valence electrons in the free neutral atoms. From Eq. (40) we calculate $e\langle\Phi\rangle$ using the tabulated wave functions and the self-consistent potentials from the Herman-Skillman tables.[31] The results for several superconducting elements, including simple (s-p) metals and transition (d-s) metals, are shown in Table I. The large values of the kinetic energy, over 100 eV for the $5d$ orbital in Ta, imply mass shifts of 100−200 ppm. From Eq. (44) we see that in totally neglecting the condensed-state interactions, errors in $\langle T\rangle_{\rm av}$ of order the Fermi energy μ are expected, about 10−20% for most superconductors as shown in Table I.

To obtain a more reliable estimate for an electron in the simple metallic solids, we performed a calculation of $\langle T\rangle$ for Be and Al using the orthogonalized-plane-wave (OPW) technique.[32] Thus

$$|\Psi_{\rm OPW}\rangle = |k_F\rangle - \sum_\alpha |\alpha\rangle\langle\alpha|k_F\rangle \tag{45}$$

and

$$\langle T\rangle = \frac{\langle\Psi_{\rm OPW}|T|\Psi_{\rm OPW}\rangle}{\langle\Psi_{\rm OPW}|\Psi_{\rm OPW}\rangle} = \frac{(\hbar^2k_F^2/2m)\left[1-2\sum_\alpha\langle\alpha|k_F\rangle^2\right]+\sum_{\alpha,\beta}\langle\beta|T|\alpha\rangle\langle\alpha|k_F\rangle\langle\beta|k_F\rangle}{1-\sum_\alpha\langle\alpha|k_F\rangle^2}, \tag{46}$$

where α and β are over the normalized atomic core states and the Fermi wave vector k_F is obtained from the bulk density. As above we actually calculate $\langle\alpha|e\Phi|\beta\rangle$ and obtain $\langle\alpha|T|\beta\rangle$ as $\langle\alpha|E'-e\Phi|\beta\rangle$, and in addition the overlap integrals $\langle\alpha|k_F\rangle$ are needed. For beryllium we calculate $\langle T\rangle=24.9$ eV ($\gamma-1=49$ ppm), and for aluminum $\langle T\rangle=32.6$ eV ($\gamma-1=64$ ppm). Both results are not very different from the estimates based on free atoms, and they support the conclusions that the expected corrections to the London moment exceed by 2 orders of magnitude the

TABLE I. Estimates for the relativistic corrections $\gamma-1$ are calculated from the Herman-Skillman tables. For each valence electron the expectation value of the potential energy $\langle V\rangle$ is numerically integrated. Then using the tabulated nonrelativistic valence energies E (NRL), $\langle T\rangle$ and $\gamma-1$ are computed using Eq. (40) or (41). All energies are given in eV. The ratio of the Fermi energy μ to the calculated $\langle T\rangle$ is also shown as an estimate of the error in $\gamma-1$.

Element	Shell	No.	$-\langle V\rangle$	$-E$ (NRL)	$\langle T\rangle$	$\gamma-1$ (ppm)	$\mu/\langle T\rangle$
Be	2*s*	2	23.6	8.1	15.5	30	0.92
Al	3*s*	2	43.3	10.0	33.3	65	0.35
	3*p*	1	23.1	4.8	18.2	35	0.64
Ti	3*d*	2	130.2	8.5	121.7	238	0.04
	4*s*	2	29.7	6.2	23.5	46	0.22
Nb	4*d*	4	114.5	6.1	108.3	212	0.04
	5*s*	1	30.6	5.4	25.1	49	0.16
In	5*s*	2	72.3	10.2	62.1	122	0.14
	5*p*	1	34.4	4.7	29.6	58	0.29
Sn	5*s*	2	111.7	12.5	99.2	194	0.10
	5*p*	2	62.6	5.9	56.7	111	0.18
Ta	5*d*	3	145.6	8.5	137.0	268	0.04
	6*s*	2	45.4	6.2	39.1	77	0.13
Pb	6*s*	2	101.1	12.1	89.0	174	0.11
	6*p*	2	55.6	5.7	49.9	98	0.19

estimated experimental accuracy. Detailed solid-state calculations using existing techniques will therefore be needed to interpret fully the measurements.

(In a recent independent calculation, Liberman has found for Ta that $\langle T \rangle = 110.8$ eV and for Pb a value of $\langle T \rangle = 74.3$ eV. Again both are in good agreement with Table I. He has used a model in which a neutral atom is embedded in an electron gas with a neutralizing positive background which possesses the same Fermi level as the metallic lattice.[33])

VII. THE ROTATING-RING EXPERIMENT

The measurements of the experiment are best understood by studying a generalized Ginzburg-Landau current-density equation

$$\vec{j} = \frac{e^*\hbar}{2i\gamma m^*}(\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi^*) - \frac{e^{*2}\psi^*\psi}{\gamma m^* c}(\vec{A} + \vec{A}_\omega) , \tag{47}$$

which includes both the effective vector potential

$$\vec{A}_\omega = \gamma \frac{mc}{e}(\vec{\omega} \times \vec{r}) \tag{48}$$

and the relativistic mass correction

$$\gamma = \left\langle \left\langle k_F \left| \frac{E - e\Phi}{mc^2} \right| k_F \right\rangle \right\rangle_{\rm av} , \tag{49}$$

where all the Fermi surface states are averaged as discussed in Sec. V. The supercurrent $\vec{j}$ is obtained from ψ, the superconductor order parameter with phase φ such that $\psi = |\psi| e^{i\varphi}$. The mass m^* and charge e^* are, respectively, $2m$ and $2e$, where the factor of 2 was first experimentally determined in 1961 (Ref. 34) and results from Cooper pairing. The density of the superconducting electron pairs is $|\psi|^2 = \frac{1}{2} n_s$, and the supercurrent velocity is proportional to $\nabla\varphi$.

Integrating around a closed path Γ contained within a multiply connected superconductor, we obtain from Eq. (47)

$$\frac{\gamma mc}{e^2 n_s} \oint_\Gamma \vec{j} \cdot d\vec{l} = \frac{\hbar c}{2e} \oint_\Gamma \vec{\nabla}\varphi \cdot d\vec{l} - \oint_\Gamma (\vec{A} + \vec{A}_\omega) \cdot d\vec{l} . \tag{50}$$

Next, requiring ψ to be a single-valued function and using Stokes's theorem, we obtain

$$\frac{\gamma mc}{e^2 n_s} \oint_\Gamma \vec{j} \cdot d\vec{l} = n \left[\frac{hc}{2e} \right] - \int_{S_\Gamma} \vec{B} \cdot d\vec{S} - \frac{2\gamma mc}{e} \vec{\omega} \cdot \vec{S}_\Gamma . \tag{51}$$

For a thick superconductor we can always find a contour Γ many penetration depths away from all surfaces. Then $\vec{j} = 0$, and for $\vec{\omega} = 0$ the expression reduces to exact flux quantization, as has been derived previously with relativistic rigor.[35] For $\vec{\omega} \neq 0$ we obtain the London moment equation (6), where now $\vec{A}_\omega$ includes the relativistic correction γ as in Eq. (48).

We wish next to derive an expression for h/m using Eq. (50). Since the cross-section area S_Γ will enter, it is necessary to use thin films, unambiguously defining S_Γ to high precision. For films that are thin compared to the penetration depth, the current density is constant. For each n we can then find an ω_n such that $\vec{j} = 0$ throughout, and thus Eq. (50) becomes

$$n \left[\frac{hc}{2e} \right] = \frac{2\gamma mc}{e} \omega_n S_\Gamma , \tag{52}$$

where we have assumed a planar geometry. For the moment, we have also assumed that the supercurrent is the only source of the vector potential $\vec{A}$. Using Eq. (52) for any two consecutive values of n, we get

$$h/\gamma m = 4 S_\Gamma \Delta\omega , \tag{53}$$

where $\Delta\omega \equiv \omega_{n+1} - \omega_n$. In the nonrelativistic limit ($\gamma = 1$), this simple relation was the original motivation for the Stanford rotating-ring experiment.

Returning again to Eq. (51), we now consider the effects of all contributions to the field $\vec{B}$, writing

$$\vec{B} = \vec{B}_s + \vec{B}_0 + \vec{B}_{\omega p} + \vec{B}_{\omega\sigma} , \tag{54}$$

where $\vec{B}_s$ is generated by the supercurrent, $\vec{B}_0$ is a constant background field, $\vec{B}_{\omega p}$ the field from static electric charges, and $\vec{B}_{\omega\sigma}$ the field from the electric dipole surface charge layers. $\vec{B}_0$ can be easily dismissed since only differences between equations of different n are used in arriving at Eq. (53), thus cancelling any constant term. Both of the remaining terms, however, vary linearly with spin speed, as does the London moment. The term $\vec{B}_{\omega p}$ originates from static electric charges on or in the rotor. Any charges on the ring can be eliminated by grounding the ring. We can derive $\vec{B}_{\omega p}$ from a vector potential,

$$\vec{A}_{\omega\rho}(\vec{r}) = \frac{1}{c}\int_V \frac{\vec{j}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}dV'$$
$$= \frac{1}{c}\int_V \frac{\rho(\vec{r}\,')\vec{\omega}\times\vec{r}\,'}{|\vec{r}-\vec{r}\,'|}dV'$$
$$= \frac{1}{4\pi c}\int_V \frac{(\vec{\omega}\times\vec{r}\,')\nabla^2\Phi(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}dV' , \quad (55)$$

where the integration extends over the volume V of the rotor and $\rho(\vec{r}\,')$ is the charge density. Averaging the current over one revolution of the rotor, only the azimuthal component remains, and Eq. (55) can be written as

$$\vec{A}_{\omega\rho}(\vec{r}) = \frac{\vec{\omega}\times\vec{r}}{c}\Phi_{\rm eff}(\vec{r}) , \quad (56)$$

where the effective electrostatic potential $\Phi_{\rm eff}$ is given by

$$\Phi_{\rm eff}(\vec{r}) = \left| \int_V \frac{\rho(\vec{r}\,')\vec{r}\,'dV'}{r\,|\vec{r}-\vec{r}\,'|} \right| . \quad (57)$$

$\vec{B}_{\omega\rho}$ can be measured by observing the field as a function of spin speed with the rotating ring above its transition temperature.

The contribution $\vec{B}_{\omega\sigma}$ from electric dipole surface layers originally suggested by Josephson[17] (and more recently by Brady[36]) can also be included in Eq. (55) and (56), but is best understood by noting that a strong magnetic field $\vec{B}_{\omega\sigma}$ is formed within the surface dipole layer. Consider a superconductor spinning about an axis of rotational symmetry. Its average electrostatic potential is constant within the lattice and zero outside, linearly changing over a distance d (~ 5 Å) through the surface dipole layer. We see that this geometry corresponds to an inner positive-charge sheet followed by a surface negative-charge sheet a distance d apart. Each has surface charge density σ such that $\Phi_{\rm in}$, the inner electrostatic potential, is given by

$$\Phi_{\rm in} = 4\pi\sigma d , \quad (58)$$

where $\Phi_{\rm out} \equiv 0$. Under rotation the charge sheets become current sheets, and we have

$$B_{\rm in} - B_{\omega\sigma} = -\frac{4\pi}{c}j = -\frac{4\pi}{c}(\sigma\pi a) = -\frac{\Phi_{\rm in}\omega}{c}\frac{a}{d} , \quad (59)$$

where we have assumed a radius a at the surface. Note that $B_{\rm in}$ ($=B_{\rm out}$) is small since the field must return to its original value after the second layer and that $B_{\rm in} << B_{\omega\sigma}$. Thus to a good approximation,

$$B_{\omega\sigma} = \frac{\Phi_{\rm in}\omega}{c}\frac{a}{d} , \quad (60)$$

and the flux through the dipole layer is

$$\int \vec{B}\cdot d\vec{S} = \frac{2\omega\Phi_{\rm in}}{c}\pi a^2 , \quad (61)$$

which in general becomes

$$\int_{\substack{\rm dipole\\ \rm layer}} \vec{B}\cdot d\vec{S} = \frac{2\phi_{\rm in}}{c}\vec{\omega}\cdot\vec{S}_\Gamma . \quad (62)$$

The vector potential from this field does not contribute to the supercurrent $\vec{j}_s$ because $d << \xi$, where the coherence length ξ is about equal to the Cooper-pair radius. However, since the rotating-ring supercurrent is measured with a sensing loop outside of its surface dipole layer, the dipole-layer flux is detected by the readout. Note that for noncylindrical geometries, although $B_{\rm in} << B_{\omega\sigma}$, $B_{\rm in}$ is not zero and in fact the flux through the entire cross section is of order the dipole-layer flux. However, the vector potential corresponding to $B_{\rm in}$ extends throughout the superconductor and is thus "sensed" by the supercurrent and driven to zero.

We now combine Eqs. (51), (56), and (62) to obtain

$$n\left[\frac{hc}{2e}\right] = \frac{2\gamma mc}{e}\left[1 - \frac{e\Phi_{\rm in}}{\gamma mc^2} + \frac{e\Phi_{\rm eff}}{\gamma mc^2}\right]\vec{\omega}_n\cdot\vec{S} , \quad (63)$$

or

$$h/m' = 4S_\Gamma \Delta\omega , \quad (64)$$

with

$$m' = m\left[1 + \frac{\langle T\rangle_{\rm av}}{mc^2} - \frac{e\Phi_{\rm in}}{mc^2} + \frac{e\Phi_{\rm eff}}{mc^2}\right] , \quad (65)$$

where we have substituted for γ from Eq. (41) and then kept only first-order terms in energies divided by mc^2. This equation is directly applicable to the experimental results. For $\Phi_{\rm eff} < 1$ V, as expected from preliminary measurements, a small correction of less than 2 ppm will result. The inner crystal potential $\Phi_{\rm in}$ is predominantly a bulk property of solids as first discussed by Bethe[37] and later by Tull,[38] and has a value between 10 and 20 eV for nearly all solids producing negative corrections of 20–40 ppm. It may be estimated by neglecting condensed-state interactions and smaller surface effects using the Herman-Skillman tables and the Bethe relation

$$\Phi_{\text{in}}=4\pi\frac{2\pi}{3}N\int_0^\infty n(r)r^4dr\ , \quad (66)$$

where N is the number of atoms per unit volume and $n(r)$ is the total electron density for each atom. Approximate values of $e\Phi_{\text{in}}$, good to 10–20%, for each of the elemental superconductors in Table I are shown in Table II, and combined to give overall estimates for m'/m. We find the $\langle T\rangle_{\text{av}}$ term is typically 5–10 times larger than $e\Phi_{\text{in}}$ resulting in a mass *increase* approaching several hundred ppm.

The experiment now under way at Stanford will make measurements on 50-mm-diameter rings, 200 Å thick by 15 μm wide, deposited on precision quartz rotors. These are levitated and spun using helium gas, and modulated through their transition temperatures to measure varying values of n. In Eq. (64) S_Γ is known to 2 ppm and $\Delta\omega$ will be measured to better than 1 ppm.

TABLE II. Estimates of the total relativistic mass shifts for elemental superconductors based on the expectation values of the kinetic energy from Sec. VI and approximate values of the inner potential.

Element	T (eV)	$e\Phi_{\text{in}}$ (eV)	$m'/m-1$ (ppm[c])
Be	25[a]	16	20
Al	33[a]	12	40
Ti	73	13	120
Nb	92	16	150
In	51	12	80
Sn	78	11	130
Ta	111[b]	19	180
Pb	74[b]	12	120

[a]From OPW calculation.
[b]From Liberman calculation.
[c]To nearest 10 ppm.

VII. CONCLUSIONS

In conclusion, the relativistic theory for rotating superconductors presented here predicts that corrections of several hundred parts per million to the classical value of the London moment should be observed in rotating-ring experiments. Already, independent experimental measurements[39] allow the calculation of Planck's constant divided by the free electron mass, with an uncertainty of 0.2 ppm through the relation

$$\frac{h}{m_e}=\frac{c\alpha^2}{2R_\infty}\ , \quad (67)$$

where α is the fine-structure constant and R_∞ the Rydberg constant. Thus a comparison of rotating superconductor measurements with the accepted value of Planck's constant divided by the free-electron mass yields for each material the expectation value of the kinetic energy for the conduction electrons averaged over the Fermi surface. This quantity is not measured directly by any other technique. Detailed solid-state calculations using existing techniques are needed to obtain accurate theoretical values which are to be compared with the experimental results. These together with the experimental measurements will also yield an independent value for h/m_e approaching a resolution of several parts per million or better.

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