Critical Size of Small Particles for the Development of Resonances

Gerd Bergmann

Department of Physics, University of Southern California, Los Angeles, California 90089-0484

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It has been often claimed that the formation of a Kondo ground state requires a minimum particle radius of $r \gg \zeta_R = \hbar v_F/\Delta$, where $\Delta = k_B T_K$ is the width of the Kondo resonance. We suggest that this minimum size is an artifact of the high symmetry of the sphere for which these calculations have been performed. A similar argument applies to other resonances. This question of minimal size is investigated for a Friedel resonance in two geometries, a sphere and a parallelepiped with a noninteger ratio of its edge lengths. A numerical calculation shows that the minimum linear size of the sample can be much smaller than ζ_R.

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Wilson [1] found in his renormalization approach to the Kondo ground state that the critical transition to an infinitely strongly bound singlet state occurred only when the radius of his sample became larger than $\zeta_R = \hbar v_F/\Delta$, where $\Delta = k_B T_K$ is the width of the Kondo resonance. This criteria has been often recounted since then and accepted by a majority in the solid-state community (see, for example, [2]). In a recent publication by Chen and Giordano [3] the authors believe that they found experimental evidence for this criteria. They investigated the Kondo effect in thin films and found a change of the logarithmic anomaly when the film thickness was reduced below the critical length scale ζ_R.

The essential physical origin of this critical size is the fact that the Kondo effect creates a resonance at the Fermi energy whose width is of the order of $\Delta = k_B T_K$. The electrons can only feel this resonance when their energy spacing is sufficiently small so that a wave packet with an energy width much less than $k_B T_K$ can be constructed which can test the width of the resonance.

If the Kondo impurity is positioned in the center of a sphere then it couples only to the free-electron states in the sphere with a fixed quantum number of angular momentum. (In the theoretical model calculation one generally considers the quantum number zero while for a realistic impurity one has instead the quantum numbers two or three.) The energetic distance of these states is $\delta = \hbar v_F \pi/R$, where R is the radius of the sphere. All the other states with different angular momenta do not couple to the impurity. The high symmetry of the sphere dramatically "dilutes" the states which couple to the impurity. The fraction of these states is very small, only about $N^{-2/3}$, where $2N$ is the total number of electrons. If we have, for example, a sphere with 10^9 electrons only about 10^3 electrons interact with the impurity. In a less symmetrical geometry the impurity couples to a much larger fraction of states. For example, in a perpendicular parallelepiped one out of eight electron states couple to an impurity located in its center. This means that in a parallelepiped one needs only a total of 10^4 electrons to obtain the same number of coupled electrons as in a sphere with 10^9 electrons. Therefore one expects that the minimal sample size of the Kondo effect is much smaller for a parallelelepiped and other geometries than for a sphere.

With respect to the minimal sample size the Kondo effect is not different from a simple Friedel resonance in the center of a sphere. Let us consider the following situation in which the conduction electrons φ_k are coupled to a localized state φ_0 with the energy ϵ_0. The φ_k are radial wave functions with angular momentum $l=0$. The resonance state φ_0 is orthogonal to the φ_k. The system can be described by the Hamiltonian

$$H = \sum_k \epsilon_k c_k^* c_k + \epsilon_0 c_0^* c_0 + \sum_k [V_{0k} c_0^* c_k + V_{0k}^* c_k^* c_0] . \quad (1)$$

The c_k, c_k^* are the annihilation and creation operators of the radial wave functions. The V_{0k} are the matrix elements between the resonance state and the φ_k. According to Friedel [4] and Anderson [5] this coupling yields a broadening of the resonance state with a smeared density of states,

$$g_R(\epsilon) = \frac{1}{\pi} \frac{\Delta}{(\epsilon - \epsilon_0)^2 + \Delta^2}, \quad \Delta = \pi \langle V_{0k}^2 \rangle g_0 , \quad (2)$$

where g_0 is the density of states of the host for one spin direction and the angular momentum $l=0$.

For this resonance problem one has the same requirement that the size of the sphere has to be much larger than the "resonance length" $\zeta_R = \hbar v_F/\Delta$. Only then are there enough states within the resonance width to build a wave packet with an energy width less than the resonance.

This means that with respect to the minimal size of the sample we have an analogous situation for the Kondo effect and the much simpler Friedel resonance. Therefore the Friedel resonance is a good model to check whether this minimal sample size is real or only a theoretical artifact due to the high symmetry of the sphere (which makes the theoretical investigations simpler).

The purpose of this paper is to compare the influence of sample size for two geometries, the sphere and the perpendicular parallelepiped with a noninteger ratio of edge lengths. (In the following we call the perpendicular

parallelepiped a "brick.") The above Hamiltonian (1) describes both systems. The essential difference is that the value for V_{0k} and the level separation is different in the two geometries. We compare both geometries containing $2N$ electrons. The volume of the brick and the sphere is $\mathcal{V}=2N\Omega/z$, where Ω is the atomic volume and z is the valence of the metal. The square of the matrix elements is $|V_{0k}|^2=|V_0|^2\Omega/|\varphi_k|^2$ (i.e., V_0 is calculated for the atomic volume Ω).

We have for the brick the quantization of the wave vectors $k_{\nu,i}=n_\nu\pi/L_i$, and the density of states per spin is, in an average, $g(\epsilon)=3N/2\epsilon$. However, only the states with odd quantum numbers have a finite amplitude, $|\varphi_k(0)|^2=(8/\mathcal{V})^{1/2}$, at the center of the brick. As a consequence the effective average level spacing is $\delta_{\rm avg}=16\epsilon/3N$, and the effective matrix element is $|V_{0k}|^2=8|V_0|^2z/2N$.

On the other hand, one has for the sphere the quantization of the radial wave number $k_r=n_r\pi/R$; the level spacing is $\delta=\hbar k\pi/mR=\epsilon/2n_r$, and the wave function at the origin is $|\varphi_k(0)|^2=k_r^2/2\pi R$. This yields the effective matrix element $|V_{0k}|^2=|V_0|^2 3z/2n_r$. The radial quantum number at the Fermi energy is $n_r=(9N/2\pi^2)^{1/3}$.

In both cases we find for Δ the value $\Delta/\epsilon_F=3\pi z|V_0/\epsilon_F|^2/4$. In the numerical calculation we take as the input the number of electrons and the width of the resonance in units of the Fermi energy Δ/ϵ_F. All other parameters follow from this input or cancel in the calculations.

The new energy eigenvalues E_n of the Hamiltonian fulfill the relation

$$E_n-\epsilon_0-\sum_k\frac{|V_{0k}|^2}{E_n-\epsilon_k}=0\,, \tag{3}$$

and the eigenfunctions are

$$\Psi_n=\frac{1}{A_n}\sum_k\frac{V_{0k}}{E_n-\epsilon_k}\varphi_k+\frac{1}{A_n}\varphi_0\,,$$
$$A_n^2=1+\sum_k\frac{|V_{0k}|^2}{(E_n-\epsilon_k)^2}\,. \tag{4}$$

Equation (3) was solved numerically. The resonance width was chosen as $\Delta/\epsilon_F=0.01$. From Δ and δ one obtains the matrix element V_{0k}. We set $V_{0k}=0$ outside of the energy range $\epsilon_F\pm 6\Delta$. The resonance energy is positioned exactly at the Fermi energy.

First we consider an artificial spectrum with equal spacing. After determining the new energies one obtains the new density of states from the inverse of the new level spacing. The additional resonance density of states nicely follows Eq. (2). [As a consequence of the finite-energy range $\epsilon_F\pm 6\Delta$ the resulting resonance width Δ is 13% larger than Eq. (2) predicts.]

For nonequal level spacing the definition of $g_R(\epsilon)$, the change in the density of states, is more difficult since the "unperturbed" density of states is dramatically fluctuating. However, the "occupation" of the resonance state as a function of energy describes the broadening of the resonance state; the occupation increases with energy E_n as

$$\langle n_0(E)\rangle=\sum_{E_n<E}\frac{1}{|A_n|^2}\,. \tag{5}$$

The condition that the radius of the sphere should be much larger than ζ_R translates into a condition for the number of electrons: $N_{\rm el}\gg(\epsilon_F/\Delta)^3$. Since we choose $\Delta/\epsilon_F=0.01$ we find for the sphere that the number of electrons should be much larger than 10^6. An additional factor of 10 in the linear relation, which translates into a factor 10^3 for the number of electrons, is required to get a reasonably smooth occupation curve for the sphere. The results for a sphere with $2N=10^9$ electrons is plotted in Fig. 1 as the staircase curve.

For the brick we choose a ratio of corner lengths of 1:1.002:1.009. The purpose of this ratio is to avoid degeneracy of energy eigenvalues. This is the closest approach to an irregular body which we can achieve with the simple geometry of a brick. The full curve in Fig. 1 shows the occupation of the resonance for a brick with only 5×10^4 electrons. This curve is so close to the occupation for an infinite sample that we omit the curve for the latter one.

The main result of this evaluation is that a brick with 5×10^4 electrons agrees as well (or even better) with the asymptotic result as does a sphere with 10^9 electrons. Clearly the critical size for the brick is much smaller than that of a sphere of $10\zeta_R$.

Besides the occupation one also likes to examine the thermodynamic properties of the resonance. As an example, we calculate the contribution of the resonance to the electronic specific heat. The resonance should contribute

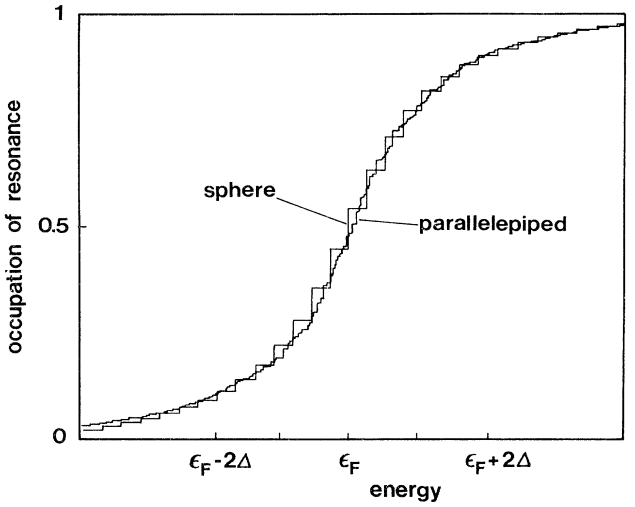

FIG. 1. The occupation of the resonance as a function of temperature. The staircase curve represents a sphere containing 10^9 electrons and the other curve, a brick with 5×10^4 electrons.

to the specific heat the term

$$c_R = \sum_n \frac{E_n}{\exp[E_n/k_BT]+1} - \sum_n \frac{\epsilon_n}{\exp[\epsilon_n/k_BT]+1} . \quad (6)$$

For temperatures far below Δ/k_B this yields a contribution of $c_R = \pi k_B^2 T/3\Delta$ per spin. However, a sample of finite size has a finite level spacing δ, and the specific heat decreases exponentially at very low temperatures. In this temperature range one expects, of course, deviations for the small sample from the above limit.

Originally the resonance energy ϵ_0 was placed in the center between two levels (i.e., at the Fermi energy of the free-electron system). To keep the Fermi energy (at $T=0$) at this position the number of electrons in the electron system with resonance is increased by $\frac{1}{2}$ per spin. Furthermore, the small sample size requires that the specific heat is calculated for constant electron number instead of constant chemical potential. Particularly for the brick this is an essential requirement because the fluctuations in the level spacing cause a considerable temperature dependence of the chemical potential.

In Figs. 2(a) and 2(b) the normalized c_R/T, i.e., $c_R/(\pi k_B^2 T/3\Delta)$ is plotted versus k_BT/Δ. The dotted curve gives the result for an infinite sample. Figure 2(a) shows the result for spheres containing 10^9, 10^{10}, 10^{11}, and 10^{12} electrons. The level spacing δ in units of Δ, i.e., δ/Δ, reduces with increasing electron number, taking the values 0.288, 0.134, 0.062, and 0.029. One recognizes that the spheres show the correct temperature behavior (for $k_BT > \delta$). At $k_BT < \delta$ the specific heat shows, of course, a completely different temperature behavior. [Since the resonance and the Fermi energy (at $T=0$) were always positioned into the center between levels, the resonance-free sample has a higher specific heat at $k_BT < \Delta$.]

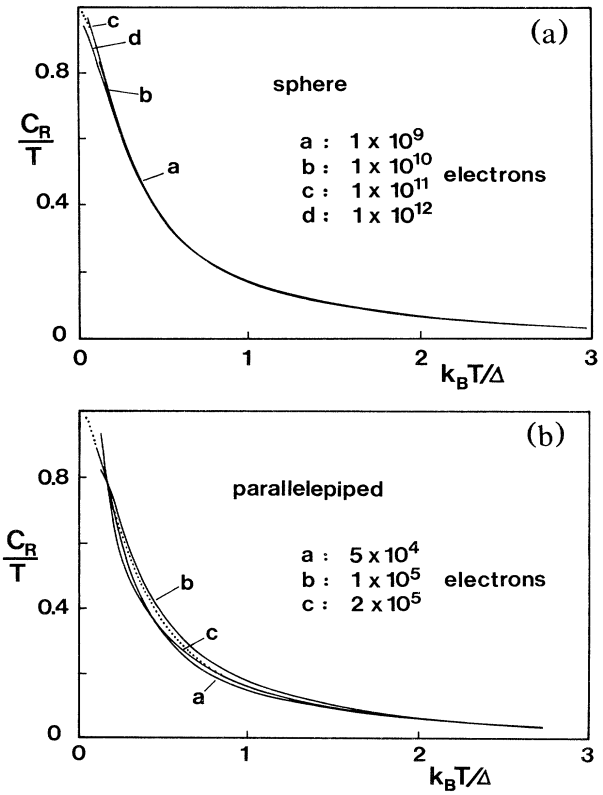

FIG. 2. (a),(b) The normalized specific heat c_R/T of the finite samples. (a) represents the results of spheres with 10^9, 10^{10}, 10^{11}, and 10^{12} electrons. (b) represents the results for a brick with 5×10^4, 1×10^5, and 2×10^5 electrons. The dotted curve represents the result for the infinite sample.

Figure 2(b) shows the normalized specific heat for bricks with 5×10^4, 1×10^5, and 2×10^5 electrons. One recognizes that the specific heat indeed shows a resonance contribution for much smaller size, and therefore electron number, than the sphere. However, if one compares brick and sphere with the same energy spacing, then the brick shows much stronger deviations from the theoretical curve. This is due to the fluctuations in the level spacing and varies from sample to sample.

The overall conclusion of this simulation is that the brick requires a much smaller size or edge length to develop a resonance than the theoretically suggested length ζ_R but, on the other hand, the fluctuations in the level spacing require an averaged level spacing $\delta_{\text{avg}} \ll \Delta$ to obtain reasonable agreement with the results for large samples.

So far we have discussed the formation of the resonance in a sphere and a brick. Although the brick has a much lower symmetry than the sphere its geometry is still highly symmetric. Irregularly shaped bodies or large clusters have a much lower symmetry. This will reduce the fluctuations in the level spacing. Furthermore, a sample with a short mean free path of the conduction electrons has a reduced symmetry as well. As a matter of fact, it has been pointed out in connection with universal conductance fluctuations [6] that a disordered electron system shows a very small variation in the level density. If we place the impurity (which carries the state φ_0) in the center of the disordered body and if the square of the wave function at the impurity does not vary too much for the different eigenstates, then a much smaller number of electrons is needed to develop the resonance. In this case the original condition that the radius is much larger than ζ_R, for example, $R \gg \hbar v_F/\Delta$, changes into a condition on the volume $\mathcal{V} \gg \Omega \epsilon_F/\Delta$.

Another question of interest is whether reduction of the sample dimension destroys the resonance. To check this question we consider a bar with square-shaped cross section whose height L_z is 500 times its width and depth $L_x = L_y$. Here we find already for 10^4 electrons an agreement with the predictions of the theory which is better than for a sphere with 1×10^{10} electrons. In this case the bar behaves completely one dimensionally (as the sphere)

since only one k_x and one k_y quantum number are occupied and the contribution of the z component to the energy yields the same level spacing as the k_r states in the sphere. The difference between the bar and the sphere is that in the latter only the fraction $n_r/N_{\rm el}$ couples to the impurity. The same applies for the two-dimensional case where only one dimension is restricted. Therefore the extreme case of a monolayer yields a full resonance (with a different Δ).

I believe that all the above conclusions apply also for the Kondo effect. Unfortunately, considering the complexity of the exact solution of the Kondo problem [7,8], as well as its numerical solution [1], it appears quite hard to perform a similar evaluation for the exact Kondo resonance. However, one may give the numerical solution of Wilson the following interpretation: As a consequence of the exchange interaction the electron system forms a localized state, in Wilson's notation the state f_0. This state forms a singlet state with the impurity $S_+s_- - S_-s_+$, where S_+ represents the impurity spin up and s_- the f_0 spin down and vice versa. The resonance state is the unoccupied spin component of the state f_0, which is coupled to the extended (quasifree) electron states. This coupling causes a broadening of the resonance state. This description is actually derived in more detail in the "slave-boson" model of the Kondo problem (see, for example, the review article [9]).

The requirement that the radius of the sphere R is much larger than ζ_R, i.e., the level spacing for the coupled $l=0$ states is much less than $\Delta=k_BT_K$, enters the Kondo problem at two points: (i) The formation of the localized state f_0 requires a sufficiently small level spacing δ on the energy scale of Δ and (ii) the extended states smear the resonance state only sufficiently smoothly when $\delta \ll \Delta$.

If we assume in accordance with the majority of theoretical papers that the Kondo impurity has a δ-like exchange potential, then it couples in perfect analogy to the Friedel resonance to all standing waves in the brick with noninteger quantum numbers. Our conclusions apply therefore also to the Kondo effect: The critical sample size can be much smaller than $10\zeta_R$. The only requirement is that the level spacing of the extended states is much smaller than $\Delta=k_BT_K$.

It is often argued that the magnetic moment requires a screening spin cloud with a radius of, at least, ζ_R, or otherwise one has an incomplete screening of the impurity spin. If the resonance state f_0 is constructed from the eigenfunctions of the brick (or any other body form) and the impurity forms a singlet state with f_0, then this yields, of course, a perfect screening of the impurity spin within the surface of the body. There is no loss in the screening cloud.

There is an argument of Nozières [10] which, if one interprets it appropriately, confirms this conclusion. Nozières points out that within the radius ζ_R of a Kondo impurity one can place $(\zeta_R k_F)^2$ additional Kondo impurities and all of them will find their screening electron because the s electron of one impurity is (almost) orthogonal to the s electron of the other impurities, even when their distance is within ζ_R. (While Nozières uses $\zeta_R=\hbar v_F/\Delta$, I obtain from the numerical evaluation that one needs at least another factor of 10 in the characteristic length to obtain a reasonable resonance.) As a consequence, a single impurity needs $N=(10\epsilon_F/\Delta)^3$ electrons in a sphere to develop the Kondo singularity. However, it can share its volume with $(10k_F\zeta_R)^2 \simeq (10\epsilon_F/\Delta)^2$ other impurities. We might interpret this result such that the number of electrons which one needs per impurity to obtain the Kondo effect is just $10\epsilon_F/\Delta$. This means for $k_BT_K=\Delta \simeq \epsilon_F/100$ that one needs a volume with 10^9 electrons for a single impurity but one can dissolve in this volume an additional 10^6 impurities and each individual impurity needs only 10^3 electrons to compensate its moment. From this point of view it might appear less surprising that in a brick 5×10^4 electrons are needed for the compensated ground state (the additional factor is needed because the energy spectrum of the brick has a strongly varying energy spacing).

This agrees well with the results of an experiment which our group performed a few years ago [11]. In this experiment a thin sandwich was condensed consisting of a 30-atomic-layer-thick Mg film, which was covered with 0.005 atomic layer of Fe. Then the Fe was covered in different steps with increasing thickness of Mg. In each step the magnetic scattering time was measured by means of weak localization. The dephasing rate did not change with the thickness of the second Mg film (after the transition from a surface to a bulk impurity was completed). This indicates that the formation of the Kondo singlet state and the screening of the magnetic impurity was not hindered by the thin film.

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