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Condensed matter physics in the 21st century: The legacy of Jacques Friedel

## The beauty of impurities: Two revivals of Friedel's virtual bound-state concept

*La beauté des impuretés : nouveaux contextes pour le concept d'état lié virtuel*

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## ABSTRACT

Jacques Friedel pioneered the theoretical study of impurities and magnetic impurities in metals. He discovered Friedel oscillations, introduced the concept of virtual bound-state, and demonstrated that the charge on the impurity is related to the scattering phase-shift at the Fermi level (Friedel sum-rule). After a brief review of some of these concepts, I describe how they proved useful in two new contexts. The first one concerns the Coulomb blockade in quantum dots, and its suppression by the Kondo effect. The second one is the dynamical mean-field theory of strong electronic correlations.

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## R É S U M É

Jacques Friedel est l'auteur de travaux pionniers sur la physique des impuretés dans les métaux. On lui doit, outre la découverte des oscillations de Friedel, le concept d'état lié virtuel et la découverte du lien entre déphasage et charge sur l'impureté (règle de somme de Friedel). Après avoir brièvement décrit certaines de ces notions, je présente leur utilisation fructueuse dans deux contextes récents : le blocage de Coulomb dans un point quantique et sa suppression par l'effet Kondo, ainsi que la théorie de champ moyen dynamique des matériaux à fortes corrélations électroniques.

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## 1. Introduction

Jacques Friedel pioneered the theoretical study of impurities in metals. Encouraged by his thesis mentor (and future brother in law) Nevill Mott, he recognised the fundamental interest of the subject – not to mention its practical importance [1]. His own words, from a 2001 interview that I will quote several times in the following, make this very clear:

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“Mott m’a mis sur un problème fondamental, celui des impuretés. Quand on change la nature d’un atome de métal, qu’on ajoute ou retire un atome de ce cristal, comment les électrons réagissent-ils?” [2]. In just a few years, during his PhD (Bristol, 1952) [3] and in the years immediately following [4–6], he unraveled physical effects and forged key concepts which were to become classic in solid-state physics, among which: Friedel’s oscillations of the charge density around an impurity, the analysis of these problems in terms of phase-shifts, and the concept of virtual bound-state. Between 1952 and 1961, the vast majority of theoretical studies devoted to impurities in metals was performed by Friedel and his first students (André Blandin, Émile Daniel, Paul de Faget de Casteljau) [7–10], first at the “École des mines” and then at the Laboratoire de physique des solides in Orsay, which Friedel co-founded. For an attempt to analyze some of the developments of this field of theoretical solid-state physics between 1952 and 1973 with a “sociology of science” perspective, the reader may want to consult the curious and rarely quoted book and article by Giuseppe Morandi and coworkers [11,12].

By the early 1960s, it had become clear that the observation of a minimum in the temperature dependence of the resistivity of some metals containing magnetic impurities (“Kondo effect”) was a puzzle of far-reaching fundamental significance – for a review of the early experiments, see, e.g., Ref. [13]. Following Kondo’s pioneering theoretical work in 1964 [14], the topic attracted enormous international attention and became a central topic of condensed matter physics all over the world. Research on this topic at the Orsay laboratory remained very active well into the 1960s and early 1970s, with important contributions on the theory side by André Blandin, Bernard Coqblin [15,16] and Marie-Thérèse Béal-Monod [17] and, on the experimental side, by Philippe Monod [18] and Henri Alloul [19].

In this article, I would like to describe two recent revivals of magnetic impurity physics in general, and especially of the virtual bound-state concept. For an early review of this concept and of its applications by Friedel himself, see Ref. [20].

The first one is about small electronic devices known as quantum dots, in which it has been realized that an odd number of electrons trapped on the dot can act as an “artificial magnetic impurity”, and that the resulting many-body effects deeply affect the physics of the Coulomb blockade in these devices.

The second one – the dynamical mean-field theory of strong electronic correlations – carries the concepts developed for magnetic impurities outside of the context of impurity physics proper. Impurity problems are viewed there as the essential building block for constructing a mean-field theory of solids with strongly interacting electrons.

One of the distinguished strengths of deep and lasting concepts is that they can be exported well beyond the realm in which they were originally invented. I hope that these two examples will illustrate the lasting beauty of impurity physics in a manner of which Friedel would not disapprove.

## 2. Virtual bound states and phase shifts

Consider an impurity atom embedded in a metallic host, with some of its energy levels not deep enough to trap electrons into a bound state. This happens in particular when the impurity level is located within the conduction band of the host. In this case, the conduction electrons spend an appreciable time near the impurity, but the wave function is still a Bloch wave far from the impurity instead of being localized as in a bound state. Friedel recognized the importance of this situation for impurities in metals and introduced the concept of “virtual bound state” to describe it.

The simplest model for this is the following. Let us denote by  $\varepsilon_d$  the impurity level (relative to the Fermi level of a conduction electron gas, which in the following will always be taken at energy  $\varepsilon = 0$ ), by  $V$  a typical matrix element for the transfer of electrons between the conduction band and the impurity level and by  $\rho_c^0$  the conduction density of states (assumed here to be constant, corresponding to a wide band). The impurity level acquires a width given by Fermi’s golden rule:

$$\Gamma = \pi V^2 \rho_c^0 \quad (1)$$

The typical time spent by an electron on the impurity level is of order  $\hbar/\Gamma$ . The additional density of states created by the impurity at energy  $\omega$  (we set  $\hbar = 1$  in the following) counted from the Fermi level has a simple Lorentzian form:

$$A_d^0(\omega) = \frac{1}{\pi} \frac{\Gamma}{(\omega - \varepsilon_d)^2 + \Gamma^2} \quad (2)$$

The average number of electrons on the impurity level (which is not an integer, since electrons come and go from the level into the metallic host) is therefore:

$$n_d = \int_{-\infty}^0 d\omega A_d(\omega) = 1 - \frac{2}{\pi} \tan^{-1} \frac{\varepsilon_d}{\Gamma} \quad (3)$$

As expected, it varies from  $n_d = 2$  for an impurity level well below the Fermi level ( $\varepsilon_d \ll 0$ ) to  $n_d = 0$  when the level is well above. The special case  $\varepsilon_d = 0$  of an impurity level exactly at the Fermi level has an additional “particle–hole” symmetry and in this case  $n_d = 1$  (half-filled impurity level  $n_d = 1$ ).

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