Spin-Singlet Resonance State in Proton-Embedded Metals: Discovery of novel high-T_K system leading to high-T_c superconductivity

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Track 3: Phase Phenomena and Electronic Phenomena
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Outline

1. Introduction

Heavy fermion superconductors

Concept of metallic screening

2. Proton Embedded in Metals as Modeled by the Electron Gas

Transition from a positive H^+ ion to a negative closed-shell H^- ion

3. Emergence of a Spin-Singlet Resonance State

Appearance of Kondo resonance between H^+ and H^- states with T_K ~2,000K at r_s=4.

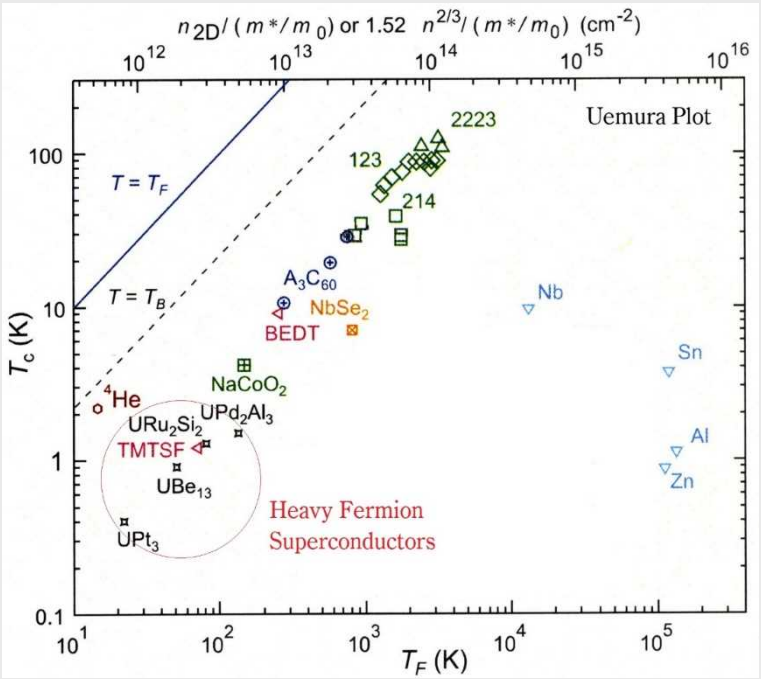
4. Summary

Heavy Fermion Superconductors

◎ T_c (and also T_F) is low, but T_c / T_F is large.

◎ Some of them are considered as Kondo-lattice systems and strong correlation exists between T_c and the Kondo temperature T_K.

Material	T_c (K)	T_K (K)
$CeCu_2Si_2$	0.7	15-20
$CePd_2Si_2$	0.43	10
$CeNi_2Ge_2$	0.2	30
$CeCu_2Ge_2$	0.6	4
$CeCu_2Si_2$	0.6	10
URu_2Si_2	1.5	60



→ Spin-fluctuation mechanism of superconductivity in the Kondo lattice;

T_c / T_K is 0.04-0.15.

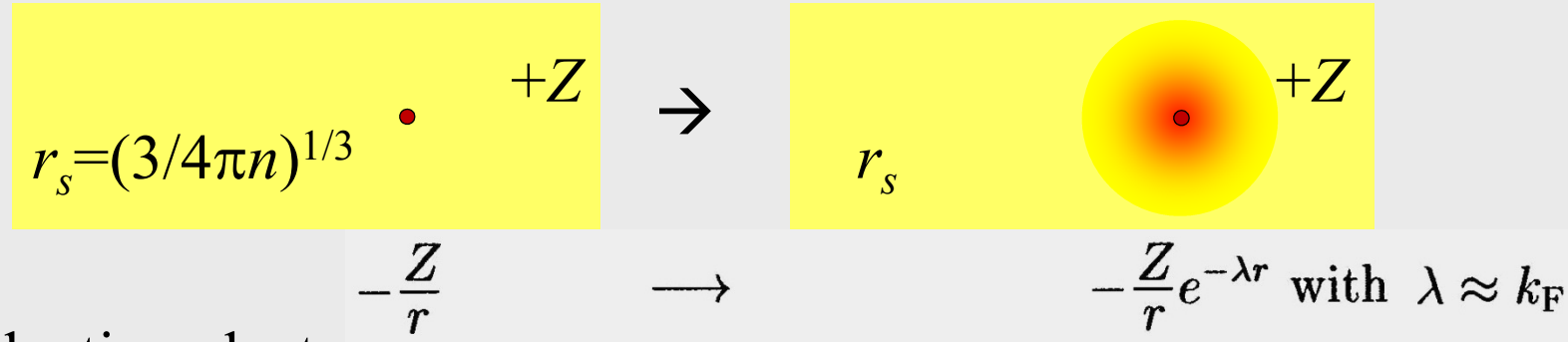
→ (1) Look for a new Kondo system with T_K >1,000K.

(2) Construct a Kondo lattice to obtain a high-T_c superconductor!

← Make all energy scales hundred times up!

Charged Point Impurity in a Metal

◎ Put an impurity of charge $+Z$ in a metal with its density n or the r_s parameter, defined by $r_s=(3/4\pi n)^{1/3}$



◉ Conduction electrons respond to screen the charge, as described by the linear-response theory (Debye-Hückel or Thomas-Fermi)

→ Charge resonance of metallic electrons and their Friedel oscillation

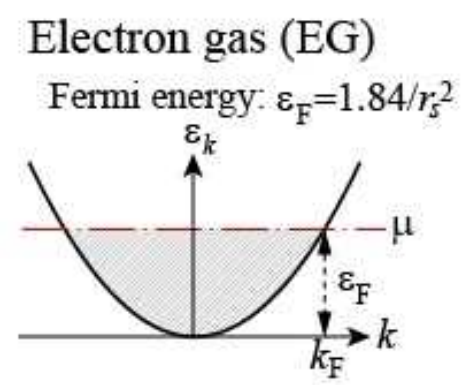
◉ Basic Question:

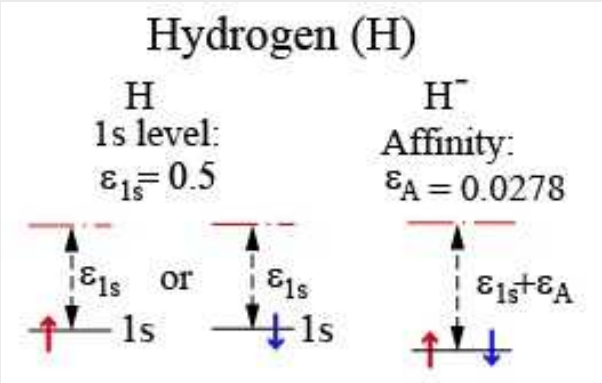
If Z is small enough, this is always a valid concept, but if Z becomes large, the effects of **nonlinear response** become important. Then, what about the effect of **spin resonance**? This spin effect is enhanced for an odd integer Z.

Proton-Embedded Electron Gas

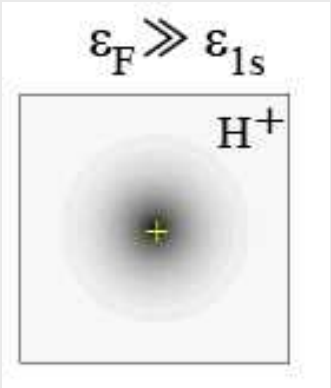
◎ Case of a proton (Z=1) embedded in the electron gas

Compare the energy scales of the electron gas and the H atom:



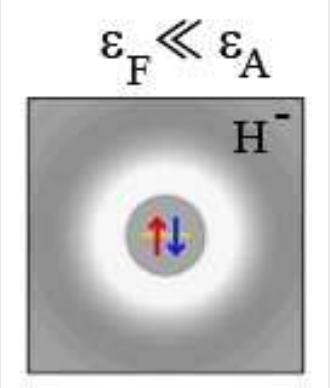


(i) r_s<2:



"Charge resonance state"
screening bare Z=1 charge

(ii) r_s>10



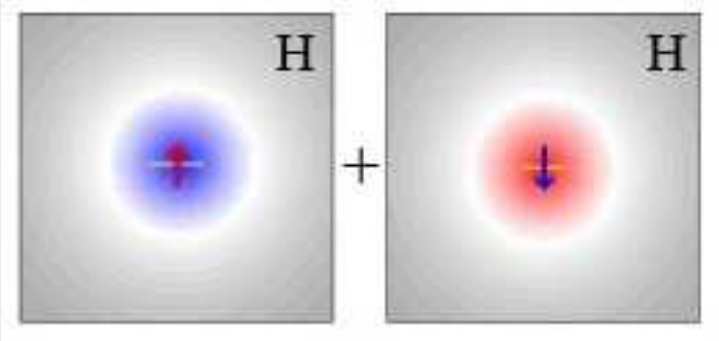
"H$^-$ ion confinement state"
screening composite Z=−1 charge

→ **What is the state in between?**

Kondo Spin-Singlet Resonance State

◎ Case of $\varepsilon_A < \varepsilon_F < \varepsilon_{1s}$:

- Naively, we may imagine a single-electron localized state with either up or down spin. → Spin polarized!
- Because of Kondo physics, this cannot be a true ground state. Rather, a **spin-singlet resonance** state is expected in which the conduction electrons at the Fermi level hybridize with the electron in the 1*s* level with changing spin orientation.



- Here the spin-screening length ξ_K is long, i.e., $\xi_K >> k_F^{-1}$.

  cf. The Thomas-Fermi screening length λ^{-1} in the charge resonance state is short, i.e., $\lambda^{-1} \sim k_F^{-1}$.

Purpose of Research

- Usually, Kondo physics is discussed in the impurity Anderson model,

$$H_{\mathrm{A}}=\sum_{\mathrm{k}\sigma}\varepsilon_{\mathrm{k}}c^{+}_{\mathrm{k}\sigma}c_{\mathrm{k}\sigma}+\sum_{\mathrm{k}\sigma}\left(Vc^{+}_{\mathrm{k}\sigma}c_{\mathrm{d}\sigma}+V^{*}c^{+}_{\mathrm{d}\sigma}c_{\mathrm{k}\sigma}\right)+\sum_{\sigma}E_{\mathrm{d}}c^{+}_{\mathrm{d}\sigma}c_{\mathrm{d}\sigma}+Uc^{+}_{\mathrm{d}\uparrow}c_{\mathrm{d}\uparrow}c^{+}_{\mathrm{d}\downarrow}c_{\mathrm{d}\downarrow}$$

but in our many-electron system with a proton at the origin of coordinates,

$$H=-\sum_{i}\frac{\nabla_i^2}{2}+\frac{1}{2}\sum_{i\neq j}\frac{1}{|\boldsymbol{r}_i-\boldsymbol{r}_j|}-\sum_{i}\frac{1}{|\boldsymbol{r}_i|}$$

(i) no predetermined localized *d* state exists;
(ii) the long-range Coulomb interaction works even among conduction electrons.

→ Must confirm the existence of the Kondo spin-singlet state in the actual proton embedded electron gas.

- Because the long-range Coulomb interaction is the origin for the charge resonance state, competition between charge and spin resonances is also an important issue to investigate.

Strategy for Confirmation

◉ Difficulties of the problem:

(i) The techniques developed for H_A cannot be applied to our H.

(ii) The Kondo-singlet wave function $\boldsymbol{\Psi_0}$ can only be constructed in the infinite system (or the total electron number $N \rightarrow \infty$), so that the Diffusion Monte Carlo (DMC) cannot be used as it is.

(iii) The DFT approach such as the LSDA calculation cannot treat such a highly correlated many-body wave function.

◉ Our basic strategy:

We focus on the ground-state electron density $\boldsymbol{n(r)}$ rather than $\boldsymbol{\Psi_0}$.

cf. In principle, it is proved that DFT can provide the exact $n(\boldsymbol{r})$ even for strongly-correlated systems.

- Check $n(\boldsymbol{r})$ in LSDA at finite N in comparison with DMC.
- Obtain $n(\boldsymbol{r})$ in either LSDA at $N \rightarrow \infty$ or extrapolation in DMC.
- Check the obtained $n(\boldsymbol{r})$ at $N \rightarrow \infty$ reproducing the behavior characteristic to the Kondo spin-singlet resonance state, or "the anomalous (shortened-period) Friedel oscillation".

Calculation Scheme: LSDA

LSDA Calculation

M. Shimomoto & K. Yoshizawa (ISSP)

Kohn-Sham scheme for single-atom embedding

$$\left[-\frac{\Delta}{2}+U_\sigma^{\mathrm{KS}}(r)\right]\phi_{i\sigma}(\boldsymbol{r})=\epsilon_{i\sigma}\phi_{i\sigma}(\boldsymbol{r})$$

$$U_\sigma^{\mathrm{KS}}(r)=-\frac{Z}{r}+\int d\boldsymbol{r}'\frac{n(\boldsymbol{r}')-n_0}{|\boldsymbol{r}-\boldsymbol{r}'|}+U_{xc}(\boldsymbol{r}\sigma;[n_\sigma(\boldsymbol{r})])-U_{xc}(n_0)$$

n_0: the uniform density of the host electron gas

$$U_{xc}(\boldsymbol{r}\sigma;[n_\sigma(\boldsymbol{r})])=\frac{\delta E^{xc}[n_\uparrow,n_\downarrow]}{\delta n_\sigma(r)},\ U_{xc}(n_0)=\frac{\delta E_{xc}^{\mathrm{LDA}}[n_0]}{\delta n_0}\ \text{and}\ n_\sigma(\boldsymbol{r})=\sum_{i(\epsilon_{i\sigma}\le\mu)}|\phi_{i\sigma}(\boldsymbol{r})|^2$$

Boundary condition for an infinite system: → Phase shift: $\delta_{l\sigma}(p)$

Write $\phi_{i\sigma}(\boldsymbol{r})=R_{pl\sigma}(r)Y_{lm}(\theta,\varphi)$,

then at $r\to\infty$, $R_{pl\sigma}\to\cos[\delta_{l\sigma}(p)]j_l(pr)-\sin[\delta_{l\sigma}(p)]n_l(pr)$

Change in the total energy associated with this embedding: δE Immersion Energy

$$\delta E=\sum_{i\sigma\in\{\text{Bound states}\}}\epsilon_{i\sigma}+\frac{1}{\pi}\sum_{l\sigma}(2l+1)\int_0^{k_F}dp\frac{p^2}{2}\delta'_{l\sigma}(p)+\int d\boldsymbol{r}\left\{\frac{Z}{r}(n_0-n(\boldsymbol{r}))\right.$$

$$\left.-\sum_\sigma U_{xc}(\boldsymbol{r}\sigma;[n_\sigma(\boldsymbol{r})])n_\sigma(\boldsymbol{r})\right\}+\frac{1}{2}\int d\boldsymbol{r}\int d\boldsymbol{r}'\frac{(n(\boldsymbol{r})-n_0)(n(\boldsymbol{r}')-n_0)}{|\boldsymbol{r}-\boldsymbol{r}'|}+E^{xc}[n_\uparrow,n_\downarrow]-E_{xc}^{\mathrm{LDA}}[n_0]$$

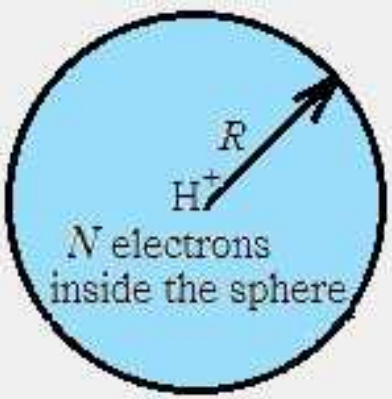
Calculation Scheme: DMC

VMC＋Diffusion Monte Carlo — Ryo Maezono (JAIST)

N-electron systems confined in a sphere of *R* (in which the embedded atom is situated at the center of the sphere) with the fixed boundary condition at the surface.

Slater-Jastrow trial function for VMC

$$\Psi\left(\vec{x}_1,\cdots,\vec{x}_N\right)=e^{J(\vec{X})}\cdot\begin{vmatrix}\psi_1\left(\vec{x}_1\right) & \cdots & \psi_N\left(\vec{x}_1\right)\\ \vdots & \ddots & \vdots\\ \psi_1\left(\vec{x}_N\right) & \cdots & \psi_N\left(\vec{x}_N\right)\end{vmatrix}$$



Jastrow factor

$$J\left(\vec{X}\right)=\sum_{i>j}u\left(r_{ij}\right)+\sum_{i,I}\chi_I\left(r_{iI}\right)+\sum_{I,j>j}f_I\left(r_{iI},r_{jI},r_{ij}\right)$$

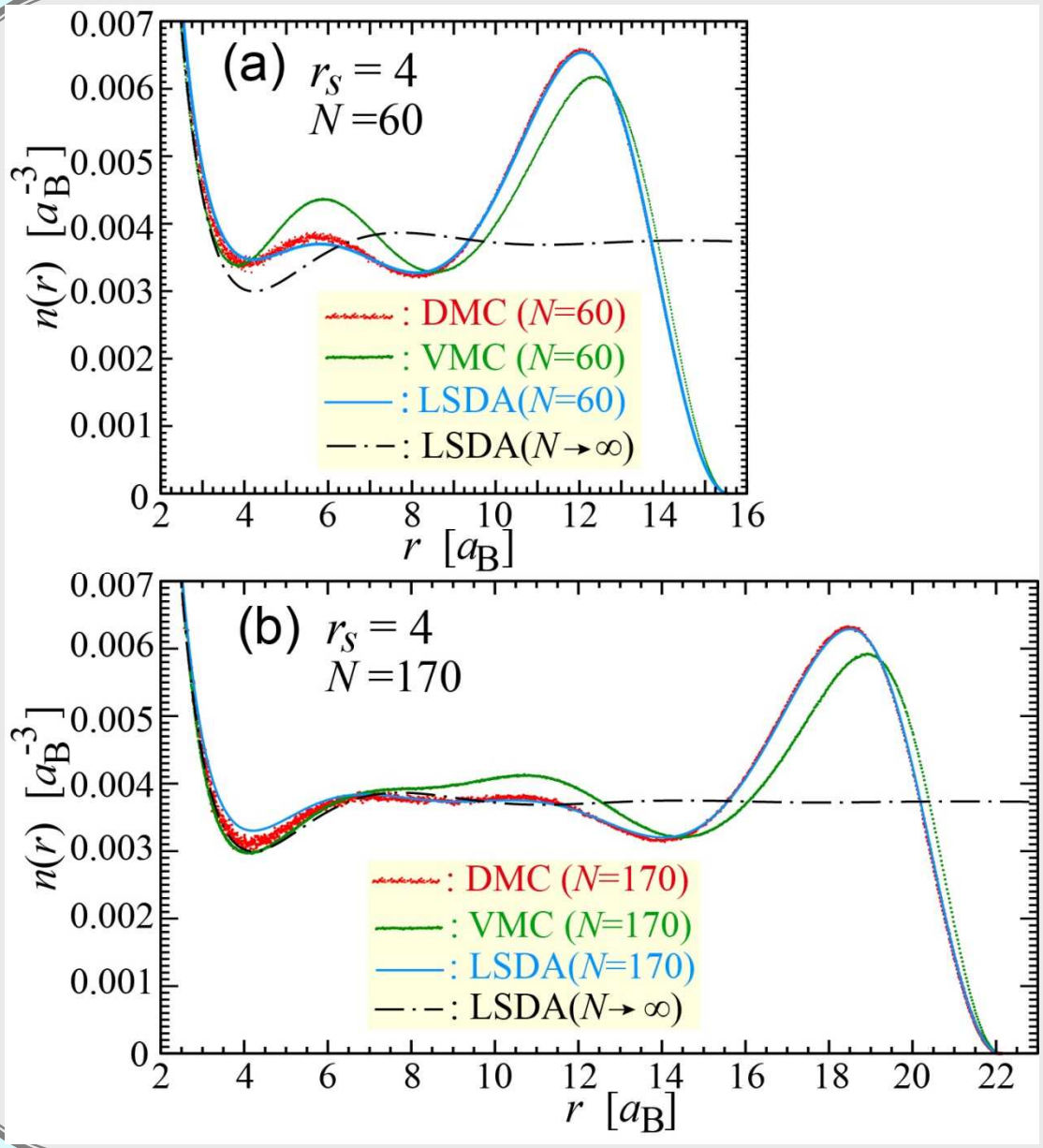
two-electron correlation — electron-proton correlation — two-electron-proton correlation

Fixed-node DMC: Casino code developed by Needs' group at Cambridge.

Mostly at *N*=58 or 60, but for checking size effects, *N* is increased up to132 and 170.

→ *N*-independent quantities are supposed to be independent of the position of fixed nodes, because the node-positions vary with *R* or *N* for a given value of r_s.

Comparison between LSDA & DMC



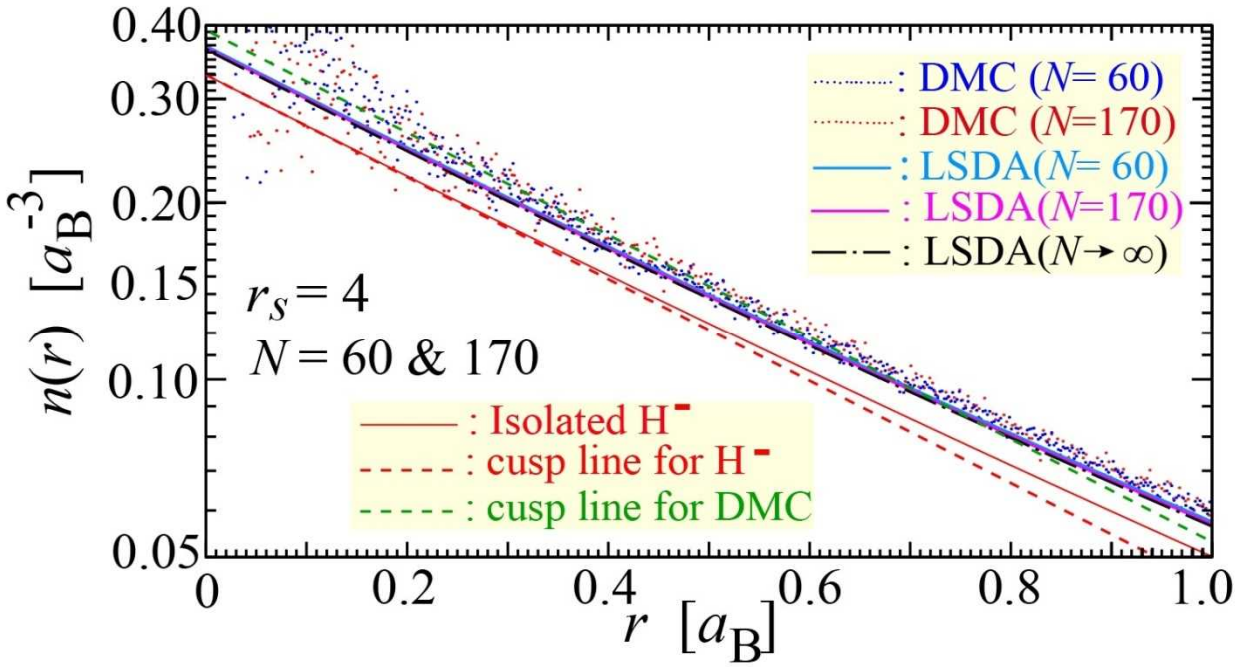
- No stable spin-polarized state is obtained in either LSDA and DMC.

  Thus LSDA gives the same results as the simple LDA.
- Rather strong N dependence is seen.

  cf. This should be, as long as R is smaller than ξ_K.
- At each N, DMC and LSDA agree surprisingly well in the whole range of $\boldsymbol{r}$, though VMC deviates much from both.

Cusp Theorem and $n(0)$

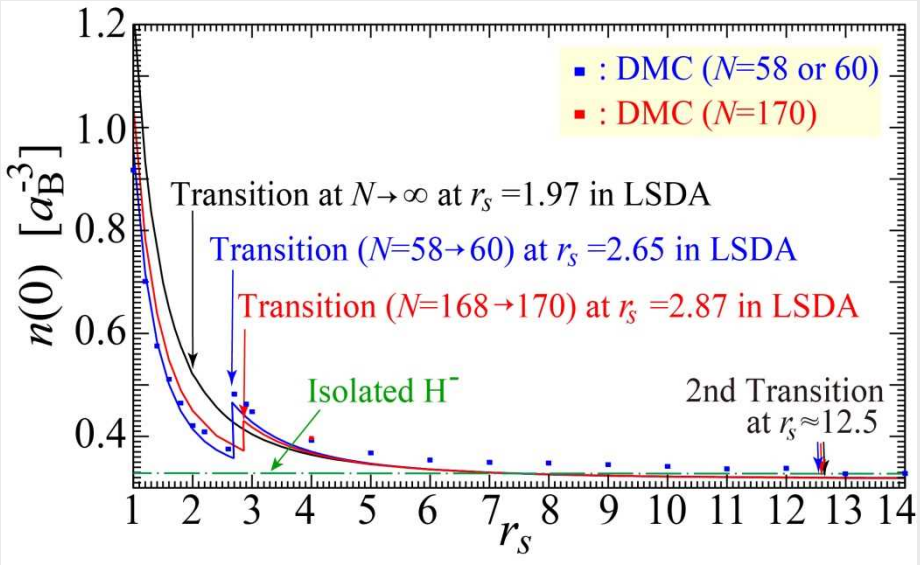
- For $r \sim 0$, **the cusp theorem** around the proton (Z=1) predicts:
  $n(\boldsymbol{r}) \sim n(0) \exp(-2Zr)$

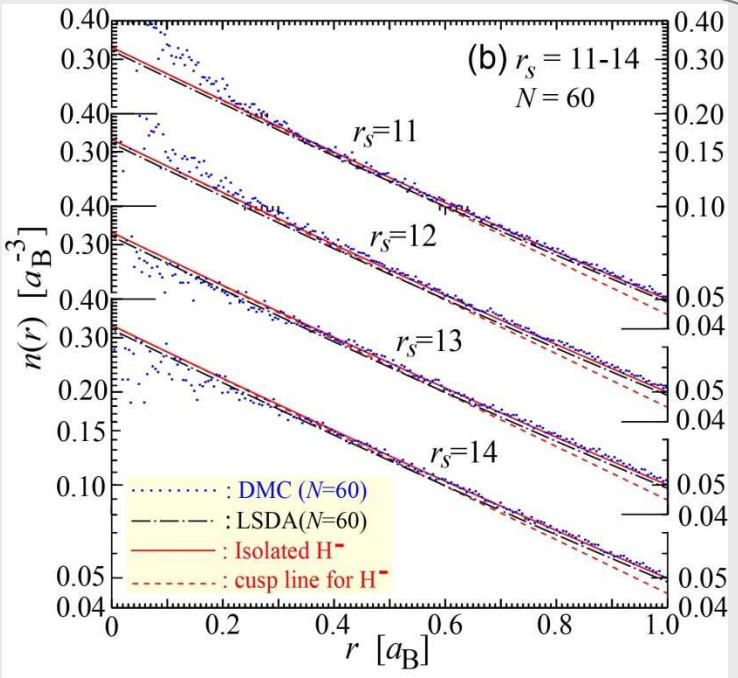


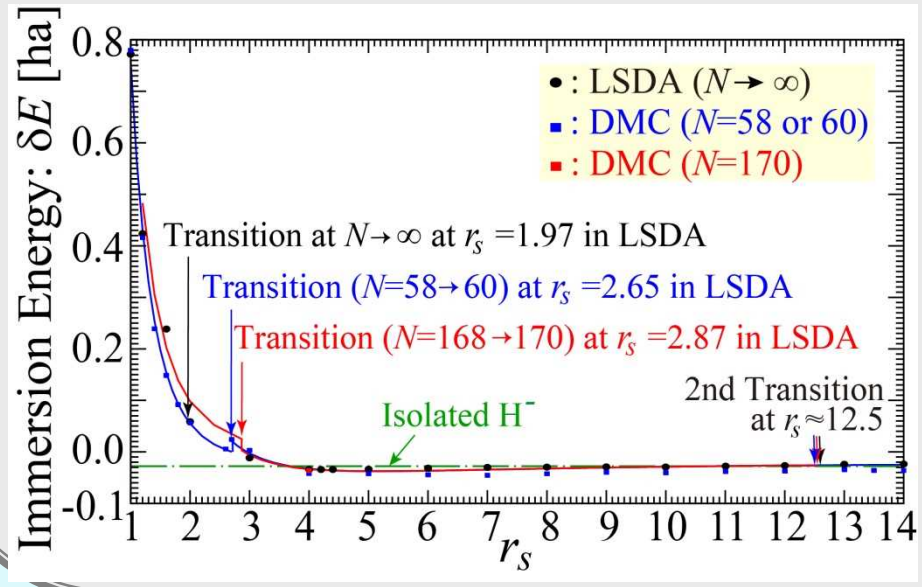
- From the cusp line in the semi-log plot, we can determine $n(0)$ accurately. For r_s=4, $n(0)$=0.395 in atomic units in DMC, while it is 0.369 in LSDA. Note that it is 0.329 for an isolated H^- ion.
- In the vicinity of r=0, N=60 is already large enough to obtain the convergent results for $n(\boldsymbol{r})$ in the limit of $N\rightarrow\infty$.

Two Sequential Transitions

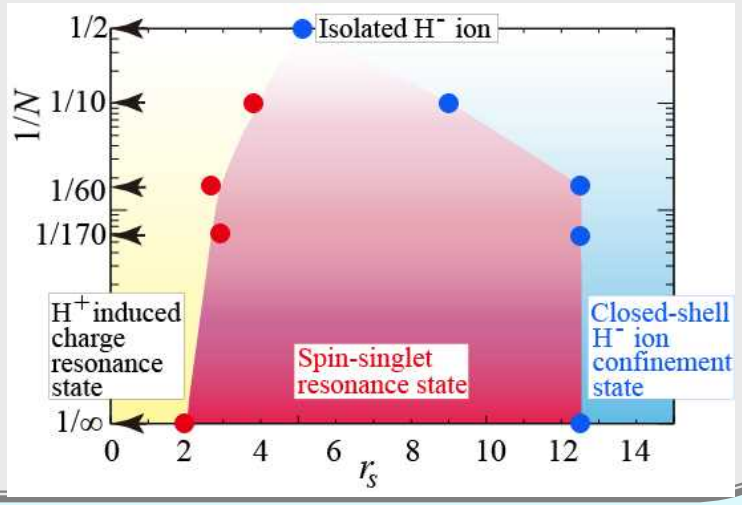
○ Plot as a function of r_s







○ Plot of the transitions in (r_s,N) space



Friedel Oscillation

○ For metals without the Kondo resonance state:

$$\lim_{r\to\infty}[n(\boldsymbol{r})-n_0]\approx\frac{1}{8\pi^2r^3}\sum_{l\sigma}(2l+1)(-1)^l\left[\cos\left(2k_{\mathrm{F}}r-\frac{3\pi}{2}+2\delta_{l\sigma}(k_{\mathrm{F}})\right)-\cos\left(2k_{\mathrm{F}}r-\frac{3\pi}{2}\right)\right]$$

Consider the s-wave part. ↓ Affleck, Borda & Saleur, PRB77, 180404(R) (2008)

○ For metals with the Kondo resonance state:

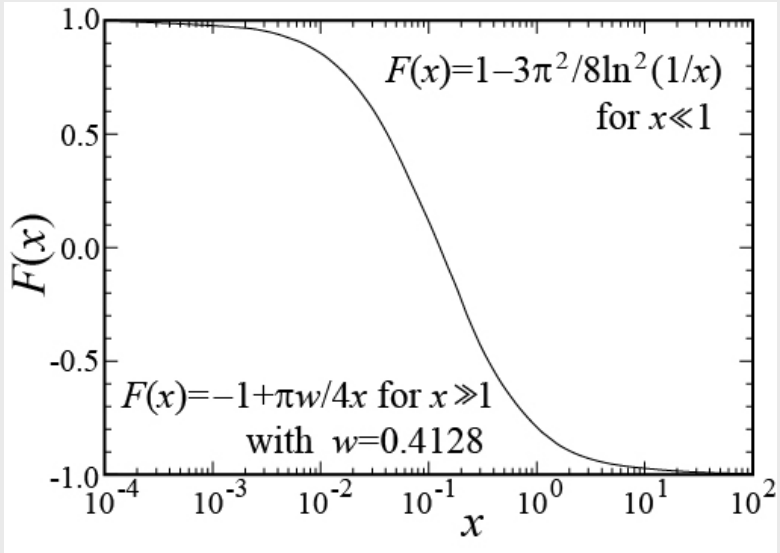
Put $F(r/\xi_{\mathrm{K}})$ here.

$$n(\boldsymbol{r})\xrightarrow[r\gg k_{\mathrm{F}}^{-1}]{}n_0+\frac{A(r)}{4\pi^2r^3}\cos[2k_{\mathrm{F}}r+\delta(r)]$$

$$A(r)=\sqrt{1-2F(r/\xi_{\mathrm{K}})\cos(2\delta_0)+F(r/\xi_{\mathrm{K}})^2},\quad \delta(r)=\tan^{-1}\left[\frac{1-F(r/\xi_{\mathrm{K}})\cos(2\delta_0)}{F(r/\xi_{\mathrm{K}})\sin(2\delta_0)}\right]$$

s-wave phase shift: $\delta_0\ [\equiv\delta_{0\uparrow}(k_{\mathrm{F}})=\delta_{0\downarrow}(k_{\mathrm{F}})]$

In accordance with the behavior of the universal function $F(x)$, $\delta(r)=\delta_0$ for $r\ll\xi_{\mathrm{K}}$, changing into $\delta(r)=\delta_0+\pi/2$ for $r\gg\xi_{\mathrm{K}}$



cf. Without the Kondo resonance state, $F\equiv 1 \rightarrow \delta(r)\equiv\delta_0$.

Anomalous Friedel Oscillation

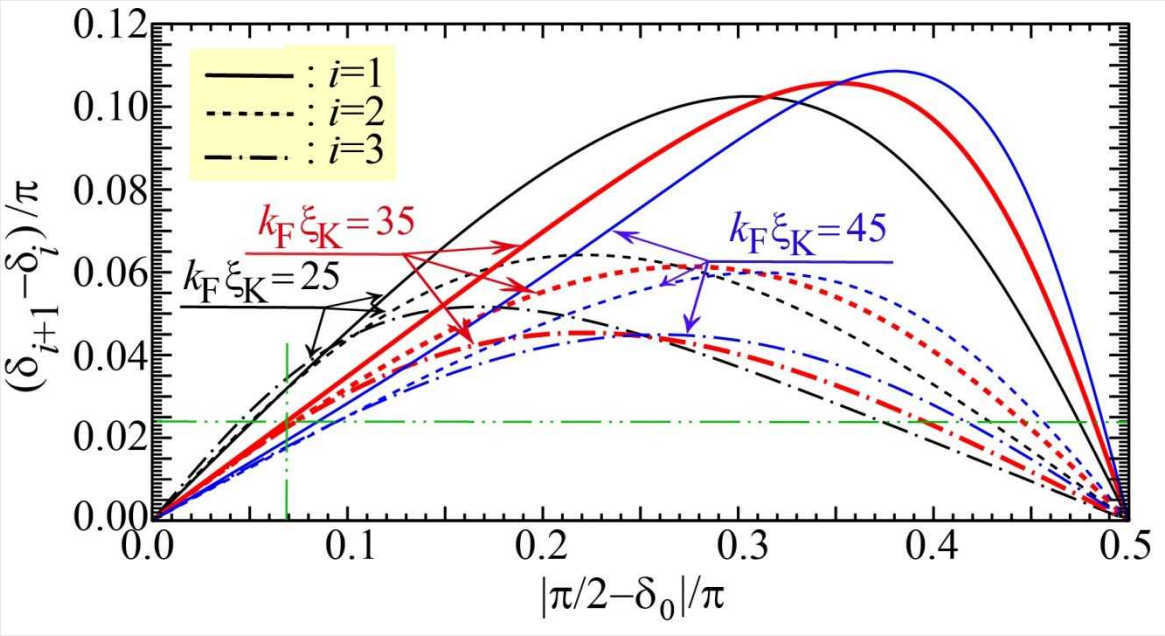
- $\delta(r)$ is a monotonically increasing function of r over ξ_K

  Write r_i as ith zero of $n(r)$-n_0: $2k_F r_i + \delta_0(r_i) = i\pi + \pi/2$

  Write r_{i+1} as $(i+1)$th zero of $n(r)$-n_0: $2k_F r_{i+1} + \delta_0(r_{i+1}) = (i+1)\pi + \pi/2$

  → $r_{i+1} - r_i = \pi \{1 - [\delta(r_{i+1}) - \delta(r_i)]/\pi\}/2k_F < \pi/2k_F$

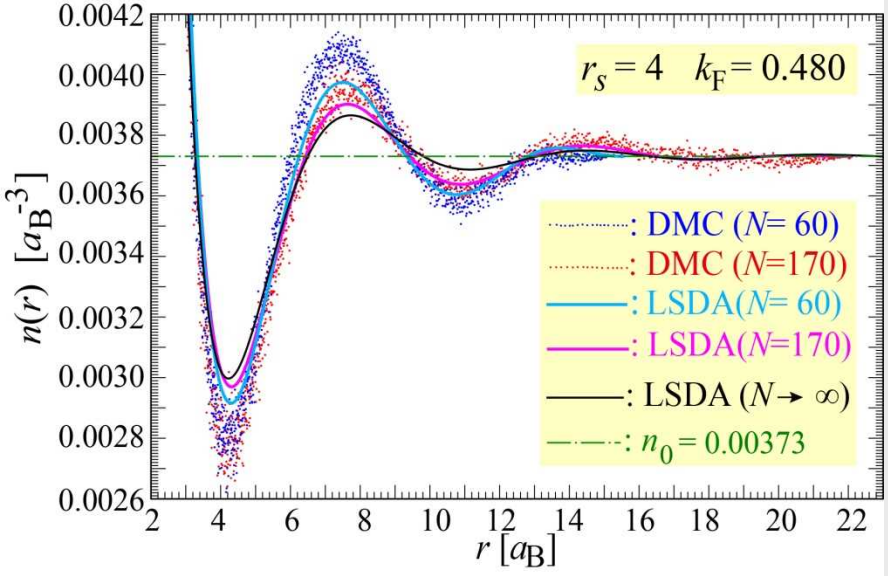
Shortening of the half period of the Friedel oscillation by the factor of $[\delta(r_{i+1}) - \delta(r_i)]/\pi$!

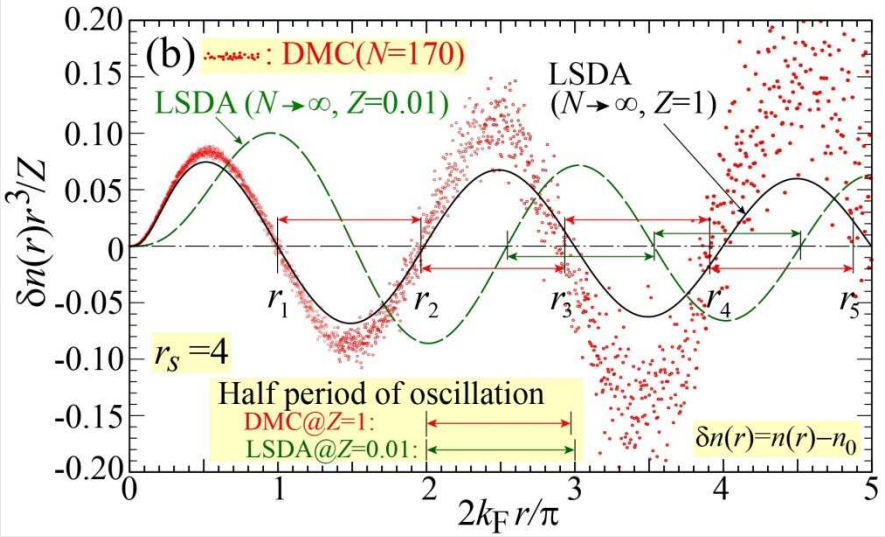


An example of the shortening factor plotted as a function of δ_0 for various $k_F\xi_K$.

First few shortening factors are enough to uniquely determine δ_0 and $k_F\xi_K$.

Shortening of the Oscillation Period in DMC

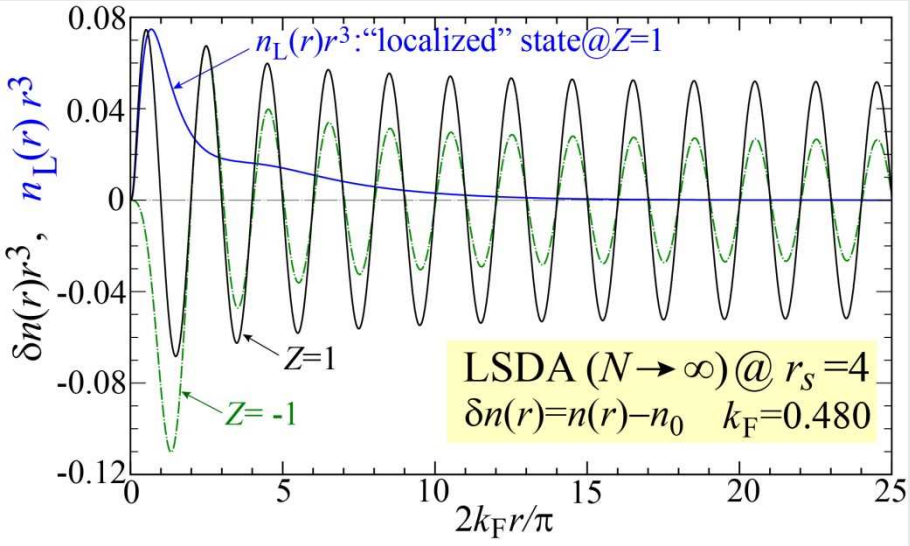




- Size correction in DMC:
  $n(\boldsymbol{r})=n(\boldsymbol{r})_{Z=1,N}-\lambda^3 n(\lambda\boldsymbol{r})_{Z=0,N-2}+n_0$
  with $\lambda = [(N\text{-}1)/(N\text{-}2)]^{1/3}$

- For $r < 13$, oscillation nodes are converged.
- The node positions are:
  $2k_F r_1/\pi = 0.994 \pm 0.005$
  $2k_F r_2/\pi = 1.970 \pm 0.008$
  $2k_F r_3/\pi = 2.949 \pm 0.013$
  $2k_F r_4/\pi = 3.927 \pm 0.019$
- The corresponding shortening factors $[\delta_{i+1}\text{-}\delta_i]/\pi$ are 0.024, 0.021, and 0.022 for i=1,2, and 3, respectively.
- These factors are consistent with the choice of $\boldsymbol{k_F\xi_K}$**~35**.

Shortening of the Oscillation Period in LDA



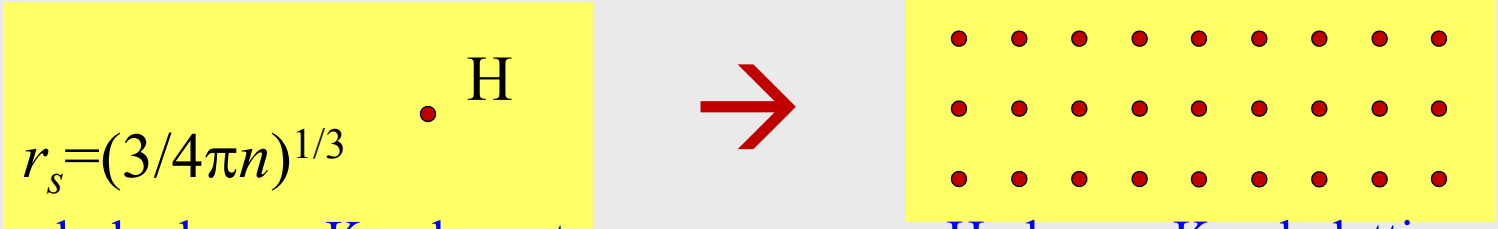
- There appears a very shallow (extending about $r \sim 80$ or $k_F r \sim 38$) 1s bound state in LSDA, but this is **not a real physical state**, but it appears only to correctly reproduce $n(r)$ in the Kondo spin-singlet resonance state.
- The shortening of the oscillation period appears as long as this shallow-state density $n_L(r)$ exists, as seen by comparison with the oscillation induced by the point charge of $Z = -1$ at the origin.
- The Kondo temperature $T_K \sim (2/k_F\xi_K)E_F$ is estimated as: $\sim$ 2100K in DMC and ~1900K in LSDA at r_s=4. Thus we cannot expect to observe the ln$T$ anomaly in the usual experiments.

Summary

1^0 Two sequential transitions in the ground state with intervening Kondo spin-singlet resonance state are clarified and identified for the proton embedding: With decreasing the metallic density, H^+ (charge resonance)→ H (Kondo resonance) → H^- (negative ion)

2^0 This result enriches the paradigm for metallic screening to a point charge of Z in the sense that, depending on the metallic density and Z, the spin resonance takes the place of the charge resonance.

3^0 By referring to heavy-fermion superconductors and by considering the astonishingly high Kondo temperature in the proton-embedded metal in the intermediate-density region, we may expect room-temperature superconductivity in a metallic hydrogen alloy, if the electron density is appropriately given.



Single-hydrogen Kondo system → Hydrogen Kondo lattice