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Electronic properties of 4f substances at configuration crossover*

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In a system of concentrated 4f ions with two configurations $4f^n$ and $4f^{n-1}$ competing for stability, a narrow resonance in the electronic density of states near the Fermi energy is expected. Using an explicitly configuration-based approach with appropriate intraconfigurational splittings included, we obtain a sum rule on the integrated density of states and a microscopic estimate of the resonance width. The width, identifiable with an interconfiguration fluctuation rate, is proportional to the nominal mixing width $\Delta(\epsilon_F) = \pi|V_{\rm mix}|^2 \rho_{\rm cond}(\epsilon_F)$, but with a proportionality factor depending rather strongly upon the specific ionic states involved. Results are obtained for electronic specific heats, x-ray photoemission linewidths, and Mössbauer spectra in such systems.

I. INTRODUCTION

In view of the large intraionic Coulomb interactions, we regard a configuration-based point of view as the physically most appropriate approach to 4f (and sometimes also 3d) ions in solids.[1-4] In the case of 4f ions, one normally has a single stable ionic configuration $4f^n$. At configuration crossover,[5] however, two configurations compete for stability and both occur with appreciable amplitudes in the many-body ground state. As first noted by Falicov and co-workers,[6,7] certain features of such a system may usefully be treated in the limit of a vanishing mixing interaction. In particular, one can discuss the thermodynamic equilibrium as a function of temperature or pressure and show that, in a concentrated system under appropriate conditions, a mixed-configuration solution is stable over a considerable range of external parameters.[5-8] In such a thermodynamic state the energy levels adjust themselves such that[5]

$$E_{n,g} - E_{n-1,g'} = \epsilon_F , \tag{1}$$

where $E_{n,g}$ and $E_{n-1,g'}$ denote the lowest ionic levels within $4f^n$ and $4f^{n-1}$, respectively, and ϵ_F is the Fermi energy. This equation implies that there is a large density of 4f electron-addition or -removal excitations in the vicinity of ϵ_F. It also indicates that there is no energy barrier opposing mixing transitions. Therefore, when a finite mixing interaction is included we expect it to induce spontaneous interconfiguration fluctuations[5] (ICF), which transfer electrons between the 4f shell of a given ion and the conduction band at a rate of the order of $\Delta(\epsilon_F) = \pi|V_{\rm mix}|^2 \rho_{\rm cond}(\epsilon_F)$, where $V_{\rm mix}$ is the mixing-interaction amplitude and $\rho_{\rm cond}(\epsilon_F)$ is the density of conduction-electron states.

A system of 4f ions at configuration crossover with finite mixing interactions presents a difficult many-body problem, for which nothing approaching a complete solution has been found. However, as will be shown in the present paper, one can obtain a useful semiquantitative characterization of certain low-energy properties of such a system by examining the spectrum of fermion excitations near ϵ_F, in the spirit of Fermi-liquid theory,[9] but from an explicitly configuration-based point of view with appropriate intraconfigurational splittings taken into account. The integrated density of fermion excitations is fixed by a sum rule, and the energy width over which they are distributed is identified with an ICF rate which is evaluated semiquantitatively. The results so obtained permit a simple understanding of various electronic properties of such a system.

II. SUM RULES ON FERMION EXCITATION SPECTRUM

According to the configuration-based approach, the many-body ground state of a system of 4f ions at configuration crossover should contain 4f parts belonging to either $4f^n$ or $4f^{n-1}$, the amplitudes of parts belonging to the remaining configurations being negligible. Furthermore, only those ionic levels lying within $\sim\Delta(\epsilon_F)$ of their respective intraconfigurational ground levels should have large amplitudes. In what follows we shall work with *ICF manifolds* containing the lowest ionic levels within the two configurations, defined such that the energy separation from excluded levels is large compared to W, where W is a total ICF width, roughly of order $\Delta(\epsilon_F)$, which will be specified later. If possible it is desirable that the spread of energies included in the ICF manifold should be small compared to W; this enables one to obtain a more complete description of the system.

In real 4f ions we have an LSJ spin-orbit ground level which usually is separated from higher levels by energies $\gtrsim 0.1$ eV, while the splitting within the

LSJ ground level from the crystalline electric field (CEF) is $\lesssim 0.01$ eV. The usual estimate of a few hundredths of an eV for $\Delta(\epsilon_F)$ in typical $4f$ systems would imply that the above conditions are reasonably well satisfied when the *LSJ* spin-orbit ground level is taken as the ICF manifold. However, the fits obtained by the present approach indicate that the ICF width W may be considerably smaller than 0.01 eV in some cases, so that an ICF manifold containing only the CEF ground level may sometimes be appropriate. In addition to realistic ICF manifolds of *LSJ* or CEF types, it is also of interest to consider hypothetical cases in which the ICF manifold includes the whole configuration or all levels within the Hund *LS* ground term.

We assume that all $4f$ ions remain equivalent in the many-body ground state of the system, i.e., that there is no tendency for the two competing configurations to establish themselves on different sublattices. (Even when all $4f$ sites are crystallographically equivalent, such a tendency might result as a consequence of sufficiently strong interionic Coulomb interactions; but there is no evidence that this occurs in the systems of interest.) Let the mean number of $4f$ electrons per ion in the many-body ground state be

$$\langle n_{4f}\rangle = n - z, \quad 0 < z < 1 . \tag{2}$$

Then the probabilities of a given ion being in $4f^n$ or $4f^{n-1}$ are $1-z$ and z, respectively.

We now consider elementary excitations which remove or add an electron to the many-body ground state $|\varphi\rangle$, leaving the system in a many-body eigenstate $|\varphi'\rangle$. It seems physically evident[9] that such elementary excitations will correspond to fermion quasiparticles when their spatial density is sufficiently small. When ICF manifolds as described above are well defined, the spectrum of quasiparticles of either removal or addition type should show a *principal band* of width $\sim\Delta(\epsilon_F)$, centered at ϵ_F, corresponding to predominantly $4f$-like excitations taking a $4f$ ion from the ICF manifold of $4f^n$ to that of $4f^{n-1}$ or vice versa. In addition to this principal band, there will generally be other bands, well separated from the principal band, corresponding to excitations leaving ions in an excited final state lying outside the ICF manifold. The latter bands are not of interest for characterizing the low-energy properties of the system, and will be excluded from our discussion. Assuming the $4f$ contributions to dominate a much smaller conduction-electron contribution, the density of removal excitations per one-ion unit cell is

$$\rho^{(-)}(\epsilon) = \sum_{\varphi' m\sigma} |\langle\varphi'|a_{m\sigma}|\varphi\rangle|^2 \delta(\epsilon - E_\varphi + E_{\varphi'}), \tag{3}$$

where $a_{m\sigma}$ is an annihilation operator for a $4f$ electron with orbital and spin azimuthal quantum numbers m and σ at some particular $4f$ ion.

Let $|n,\beta\rangle$ and $|n-1,\beta'\rangle$ denote states of the given ion belonging to the ICF manifolds of the two configurations, and let $|\xi\rangle$ denote states belonging to a set which spans the remainder of the system external to the given ion. We decompose the many-body eigenstates into direct products of such states. According to the remark following Eq. (2), the amplitudes of the many-body ground state in such a decomposition satisfy

$$\sum_{\xi,\beta} |\langle \xi; n, \beta|\varphi\rangle|^2 = 1 - z . \tag{4}$$

As will be shown below, for all cases of interest the ionic states within the ICF manifolds satisfy a relation of the form

$$\sum_{\beta' m\sigma} \langle n,\beta''|a^\dagger_{m\sigma}|n-1,\beta'\rangle\langle n-1,\beta'|a_{m\sigma}|n,\beta\rangle = Q^{(-)}_{n\to n-1}\delta_{\beta,\beta''} . \tag{5}$$

Using Eqs. (4) and (5), we obtain for the integrated density of electron-removal excitations within the principal band:

$$Y^{(-)}_{n\to n-1} = \int d\epsilon\, \rho^{(-)}(\epsilon) = (1-z)Q^{(-)}_{n\to n-1} . \tag{6}$$

For electron-addition excitations the relation corresponding to Eq. (5) is

$$\sum_{\beta' m\sigma} \langle n-1,\beta''|a_{m\sigma}|n,\beta'\rangle\langle n,\beta'|a^\dagger_{m\sigma}|n-1,\beta\rangle = Q^{(+)}_{n-1\to n}\delta_{\beta,\beta''} , \tag{7}$$

and the sum rule corresponding to Eq. (6) is

$$Y^{(+)}_{n-1\to n} = \int d\epsilon\, \rho^{(+)}(\epsilon) = zQ^{(+)}_{n-1\to n} . \tag{8}$$

(The subscripts $n\to n-1$ or $n-1\to n$ on $Y^{(\pm)}$ or $Q^{(\pm)}$ have been included for added clarity but will sometimes be dropped in later equations.)

The quantities $Q^{(\pm)}$ could be related to squared coefficients of fractional parentage, but in the cases of present interest they can be evaluated by more elementary techniques. In the case where entire configurations are included in the ICF manifolds, the expressions on the left-hand side of Eqs. (5) or (7) reduce by closure to forms involving the $4f$ number operator, and these equations are seen to hold with

$$Q^{(-)}_{n\to n-1} = n \tag{9}$$

and

$$Q^{(+)}_{n-1\to n} = N_0 - (n-1), \tag{10}$$

where $N_0 = 14$ is the capacity of the $4f$ shell. When

the ICF manifolds include all states within the LS or LSJ ground levels, we use an appropriate symmetry analysis[10] of the $4f$ creators to verify Eqs. (5) and (7). The details are given in the Appendix, and the results obtained for $Q^{(-)}_{n\to n-1}$ and $Q^{(+)}_{n-1\to n}$ are plotted as functions of n in Figs. 1 and 2. These curves show that restricting the ICF manifold within the final configuration by a new stage of intraconfigurational splitting reduces $Q^{(\pm)}$, except where the splitting vanishes trivially or where selection rules prevent it from having an effect. (As an example of the latter kind, adding a hole or electron to $4f^7\,{}^8S$ produces states with $L=3, S=3$, which occur only within the Hund term; therefore when the initial state is $4f^7$, an LS ICF manifold yields the same results for $Q^{(\pm)}$ as does an ICF manifold containing the whole configuration.) The values obtained for $Q^{(\pm)}$ are seen to vary quite strongly depending upon the particular configuration and type of ICF manifold assumed. Particularly small values, 0.143 and 0.150, respectively, are obtained for $Q^{(-)}_{7\to 6}$ and $Q^{(+)}_{5\to 6}$ with LSJ projection, as a result of the singlet LSJ ground level of $4f^6$.

The quasiparticle description applies only when the spatial density of quasiparticles relative to the original many-body ground state is small ($\ll 1$ per unit cell). This requires that $kT \ll \Delta(\epsilon_F)$. It also means that the integrated density of states within the quasiparticle principal band, $Y^{(+)}$ or $Y^{(-)}$, is not identical with the number of electrons or holes which the $4f$ shells could accommodate in a real, noninfinitesimal population change. The latter number is z or $1-z$ per ion, which can be quite different from $Y^{(+)}$ or $Y^{(-)}$ since $Q^{(+)}$ or $Q^{(-)}$ can be quite different from 1.

III. ICF RATES AND ELECTRONIC DENSITY OF STATES

In the present section we shall define and evaluate the rates of interconfiguration fluctuation induced by mixing interactions in a $4f$ system at configuration crossover, and relate these rates to the electronic density of states. The physical interpretation of the ICF rates will be further developed in the following section, where we will emphasize that at low temperatures ICF corresponds to a zero-point motion which is not always directly observable.

Whereas the sum rules derived in Sec. II are rigorous and quantitative consequences of a configuration-based treatment of appropriate systems, the results of the present section are of a more phenomenological nature and are restricted to semiquantitative accuracy. They should nevertheless yield a useful description of certain basic properties of a $4f$ system at configuration crossover.

To proceed, let us suppose that our system has initially been prepared in an uncorrelated ensemble state, such that each conduction electron or ionic level is occupied with same probability as in the many-body ground state, but without any correlations among the various conduction electron and ionic amplitudes. The zero-point ICF rate will be defined as the mean rate at which a $4f$ ion decays out of its initial configuration, as a result of the finite mixing interaction, under these conditions.

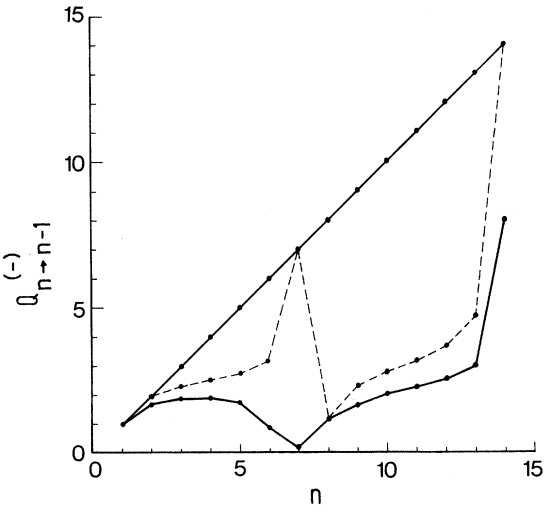

FIG. 1. Sum-rule strength $Q^{(-)}_{n\to n-1}$ for $4f$ systems where the ICF manifolds are taken as entire configurations (upper solid line), LS ground terms (dashed line), or LSJ ground levels (lower solid line).

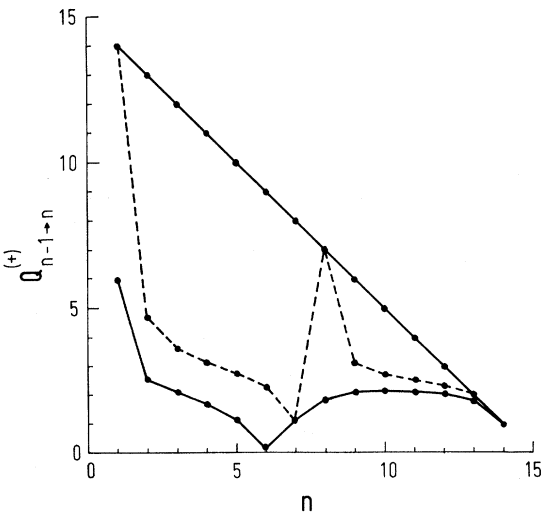

FIG. 2. Sum-rule strength $Q^{(+)}_{n-1\to n}$ for $4f$ systems. Meaning of three lines as in Fig. 1.

The mixing interaction is taken as

$$H_{\rm mix}=\sum_{km\sigma} V_{\rm mix}(a^{\dagger}_{m\sigma}c_{km\sigma}+c^{\dagger}_{km\sigma}a_{m\sigma}), \tag{11}$$

where $a^{\dagger}$ and $c^{\dagger}$ denote creators for $4f$ and conduction electrons, respectively, the latter belonging to the partial wave $l=3$. The emissive and absorptive zero-point ICF rates are then given by second-order perturbation theory as

$$W^{(-)}_{n\to n-1}=\sum_{\beta'\beta m\sigma}[1-f(\epsilon_{\beta\beta'})] \times P_{\beta}|\langle n-1,\beta'|a_{m\sigma}|n,\beta\rangle|^2 2\Delta(\epsilon_{\beta\beta'}) \tag{12}$$

and

$$W^{(+)}_{n-1\to n}=\sum_{\beta'\beta m\sigma} f(\epsilon_{\beta\beta'})P_{\beta'}2\Delta(\epsilon_{\beta\beta'}) \times|\langle n,\beta|a^{\dagger}_{m\sigma}|n-1,\beta'\rangle|^2, \tag{13}$$

where we have taken $\hbar=1$; $\epsilon_{\beta\beta'}=E_{n,\beta}-E_{n-1,\beta'}$ is the energy of the conduction electron which is emitted or absorbed; and $f(\epsilon)$ and P_{β} are the initial occupation distributions of conduction-electron and ionic states, respectively, the latter being normalized to 1 for each configuration. The distribution $f(\epsilon)$ decreases from 1 to 0 over an energy range of width $\sim\Delta(\epsilon_F)$ centered at ϵ_F, and for the contributing transitions $\epsilon_{\beta\beta'}$ lies predominantly within this same energy range. We therefore evaluate the above expressions semiquantitatively by assigning f the mean value $\frac{1}{2}$ and replacing $\Delta(\epsilon_{\beta\beta'})$ with $\Delta(\epsilon_F)$. (A more elaborate evaluation would hardly be justified, since the whole concept of a zero-point ICF rate clearly has only a semiquantitative significance.) This yields

$$W^{(-)}_{n\to n-1}=\Delta(\epsilon_F)Q^{(-)}_{n\to n-1}, \tag{14}$$

$$W^{(+)}_{n-1\to n}=\Delta(\epsilon_F)Q^{(+)}_{n-1\to n}, \tag{15}$$

where the $Q^{(\pm)}$ are the same quantities which were evaluated above.

These same Eqs. (14) and (15) are found also to give the rates of emissive and absorptive ICF at a temperature which is $\gg\Delta(\epsilon_F)$, although still small compared to the energies separating the ICF manifolds from the remaining ionic levels. In this case, we no longer need to contemplate a specially prepared initial ensemble state of the system. Instead, we consider a thermal distribution, which under the conditions just stated is approximately equivalent to uncorrelated thermal distributions of the single-ion and conduction-electron levels. The fractional thermal occupation of conduction-electron levels is $\frac{1}{2}$ in the relevant range of energies, so Eqs. (14) and (15) again result. Although the high-temperature ICF rates have the same values as the zero-point rates, they have a different physical significance, since they correspond to real charge fluctuations as opposed to zero-point motions.

It is interesting, although irrelevant to the main theme of the present paper, that expressions similar to Eqs. (14) and (15) also hold for the mixing-decay rates of excited ionic levels when a unique ionic configuration is energetically stable.[11] First let $4f^n$ be the stable configuration, and consider the mixing-decay rate of an ion which has been excited to the lowest level of $4f^{n-1}$. Consider ionic energy-level schemes such that decays of this level are energetically allowed into all states of $4f^n$, into all states of the LS ground term of $4f^n$, or into all states of its LSJ ground level. Here energetical allowedness means that the energy of the emitted conduction electron lies above ϵ_F, where we assume that kT is negligible compared to the relevant energy differences so that the Fermi distribution is effectively a step function. Assuming that $\Delta(\epsilon)=\Delta(\epsilon_F)$ for all relevant conduction-electron energies, these absorptive mixing-decay rates are given by twice Eq. (15) with the appropriate $Q^{(+)}$ values. The analogous emissive mixing-decay rates from $4f^n$ to a stable $4f^{n-1}$ configuration are given by twice Eq. (14).

The zero-point ICF rates appropriate to various configurations and various types of ICF manifold can be read off immediately from Figs. 1 and 2. The calculated rates, in terms of $\Delta(\epsilon_F)$, are seen to vary over two orders of magnitude depending upon the case considered. In contrast, a Hartree-Fock treatment of the mixing would suggest a mixing-fluctuation rate of $2\Delta(\epsilon_F)$ for all cases. If the intraionic interactions among $4f$ electrons could be neglected, then the latter result would be correct. In reality, however, there are intraionic energies large compared to $\Delta(\epsilon_F)$, which must be expected to influence the mixing-fluctuation rates. Our results indicate that this influence is quite significant.

The ICF rates discussed so far refer to the individual configurations. The single-electron $4f$ excitations of interest correspond to transitions between the ICF manifolds of the two configurations, and the principal band of quasiparticles should therefore have a width given approximately by the sum of Eqs. (14) and (15), $W=(Q^{(-)}+Q^{(+)})\Delta(\epsilon_F)$. The quasiparticles of removal or addition type lie below or above ϵ_F, respectively, and should together form a single smooth band. For definiteness we assume a Lorentzian band shape, the simplest shape consistent with the demonstrable fact that the second moment of the band shape diverges if $\Delta(\epsilon)=$const:

$$\rho(\epsilon) = (YW/2\pi)[(\epsilon - \epsilon_0)^2 + (\tfrac{1}{2}W)^2]^{-1}. \quad (16)$$

Here the integrated density is $Y = Y^{(-)} + Y^{(+)}$. Since this quantity depends upon the $4f$ population parameter z, a rigid-band picture does not apply. The position of the band center ϵ_0 relative to ϵ_F is determined by the known ratio of $Y^{(-)}$ to $Y^{(+)}$:

$$x = \frac{2(\epsilon_F - \epsilon_0)}{W} = \tan\left(\frac{\pi}{2}\,\frac{Y^{(-)} - Y^{(+)}}{Y^{(-)} + Y^{(+)}}\right). \quad (17)$$

Then the density of states at ϵ_F is

$$\rho(\epsilon_F) = \frac{2}{\pi\Delta(\epsilon_F)}\,\frac{(1-z)Q^{(-)} + zQ^{(+)}}{Q^{(-)} + Q^{(+)}}\,\frac{1}{x^2+1}. \quad (18)$$

Substituting Eqs. (6) and (8) into the expression for x, we find that $\rho(\epsilon_F)$ depends only on z and the ratio $P = Q^{(-)}/Q^{(+)}$. As can be seen from Eqs. (5) and (7), P is simply D_{n-1}/D_n, the ratio of dimensionalities of the ICF manifolds of the two configurations. The dimensionless quantity $\rho(\epsilon_F) \times \pi\Delta(\epsilon_F)$ is plotted as a function of z for various P values in Fig. 3. The value of z in a $4f$ system at configuration crossover is determined primarily by a competition of various energies large compared to the mixing energy,[5] so from the point of view of the ICF problem z can be regarded as a fixed input parameter.

The assumption of a single-peaked Lorentzian density of states, leading to Eq. (18), is applicable only when the spread of ionic energies included in the ICF manifolds is small compared to the total ICF width W. If this condition is not satisfied, our sum rules still apply, but the principal band may show incipient splitting and an expression for $\rho(\epsilon_F)$ cannot be given.

IV. OBSERVABLE EFFECTS OF ICF IN 4f SYSTEMS

The term "interconfiguration fluctuations," or its more plastic equivalent "charge fluctuations," may suggest a persistent motion in the system. One can in fact think of ICF as implying a quantum-mechanical zero-point motion which is implicit in the many-body ground state. However, in accordance with general thermodynamic principles, the noise spectrum of the undisturbed system must die out as the temperature approaches zero. Fluctuation effects corresponding to a noise output or other observable motion are therefore present only to the extent that the system is probed at finite frequencies or observed at finite temperatures. We shall illustrate these remarks by considering some specific types of measurement in the present section.

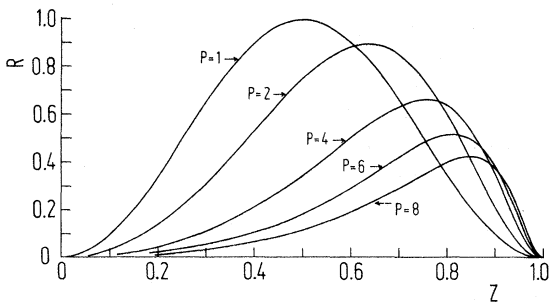

FIG. 3. Dimensionless density of $4f$ single-electron excitations, $R = \rho(\epsilon_F)\pi\Delta(\epsilon_F)$, as a function of the $4f$ population parameter z, for various values of $P = Q^{(-)}/Q^{(+)}$. Curves for $P < 1$ have been omitted for graphical clarity; they are implied by the identity $R(z,P) = R(1-z, 1/P)$.

Many properties of an ICF system at low temperatures are dominated by the thermal excitation of quasiparticles. In particular, we expect a large electronic specific heat which is linear in T with a coefficient orders of magnitude larger than in normal metals:

$$C_V = \rho(\epsilon_F)(\tfrac{1}{3}\pi^2)k^2T. \quad (19)$$

This expression applies only for $kT \ll \Delta(\epsilon_F)$, which is necessary in order that the spatial density of quasiparticles be low and also guarantees that the density of states relevant to thermal excitations be approximately constant. Such very large linear specific heats have been observed in various $4f$ systems believed to be at configuration crossover, including α-Ce,[12,13] collapsed SmS,[14] and YbCuAl,[15] whose measured coefficients are 12.8, 145, and 160 mJ/mole K^2, respectively. If ICF manifolds of LSJ type are assumed, Eqs. (18) and (19) yield $\Delta(\epsilon_F) = 0.011$ and 0.0016 eV for Ce and SmS, respectively, where we have used $z = 0.5$ and 0.6 as indicated by fits to pressure-volume curves.[5] For YbCuAl the value of z is not known and the equations yield only an upper bound $\Delta(\epsilon_F) \leq 0.0018$ eV. We have not attempted to correct for non-$4f$ contributions to the specific-heat coefficient, which probably amount to several mJ/mole K^2; such corrections could considerably increase the value of $\Delta(\epsilon_F)$ for α-Ce.

These fits based upon ICF manifolds of LSJ type imply total ICF widths $W = (Q^{(-)} + Q^{(+)})\Delta(\epsilon_F)$ of 0.077 and 0.0016 eV for Ce and SmS. For Ce, this fitted W is large compared to likely CEF splittings and indicates self-consistency, but for SmS the opposite is true. The cubic CEF has no effect on the $J = 0$ spin-orbit ground level of $4f^6$, but splits the $J = \frac{5}{2}$ level of $4f^5$ into a doublet and a quartet. If we assume a CEF splitting large compared to the true W, we can use an ICF manifold of CEF type to obtain a more realistic fit as discussed in the Appendix. This yields $\Delta(\epsilon_F) = 0.0026$ or 0.0046 eV, and $W = 0.0019$ or 0.0020 eV, for a quartet or doublet CEF ground level.

The noise spectrum of the ICF system, as measured by some weak-coupled probe, is described by a spectral density

$$J(\omega, T) = \frac{(2\pi/N_0)|I\rho(\epsilon_F)|^2\omega}{\exp(\omega/kT) - 1}, \tag{20}$$

where I characterizes the coupling between probe and ICF system and the divisor $N_0 = 14$ is included to give this coupling its most natural atomic normalization. The frequency ω is defined according to a convention whereby positive frequency corresponds to emission of energy from the ICF system. The characteristic function of ω and T results from the folding of Fermi distributions for the initial and final quasiparticle states involved in the fluctuations.[16] The expression is valid when ω and kT are both small relative to $\Delta(\epsilon_F)$, or more precisely relative to W. This noise spectrum is seen to satisfy the general considerations stated at the beginning of this section.

Mössbauer isomer-shift spectroscopy in systems at configuration crossover[17,18] offers, in principle, the possibility of measuring a spectral density of the above type. In this application the coupling constant I is defined such that the γ-frequency shift induced by a change in occupancy of the $4f$ shell is I (n_{4f} – const). At zero temperature we expect a single line (in spatially homogeneous systems), having a position determined by the mean $4f$ population and a linewidth determined by the nuclear lifetime. At temperatures which are finite, but still small compared to $\Delta(\epsilon_F)$, we expect an extra broadening simply equal to $J(0, T)$, which is seen to be linear in T. In this low-temperature regime where the quasiparticle picture is valid, the linewidth is determined not by the ICF rate itself (which is temperature independent), but by a spectral density which is temperature dependent because it involves the thermal population of quasiparticle states. On the other hand, as noted in Sec. III, at temperatures high compared to $\Delta(\epsilon_F)$ the ICF rate does describe real fluctuations in the local charge. The effect of such fluctuations on the Mössbauer spectrum can be computed by well-known methods[18]; one expects the line to broaden as the ICF rate decreases toward I, and to split into resolved lines corresponding to the two configurations as the ICF rate becomes smaller than I. Unfortunately, in real $4f$ systems at configuration crossover the ICF rate appears to be too large to permit low- or high-temperature ICF effects to be observed. The absence of an observable charge-fluctuation broadening in the high-temperature regime (i.e., at room temperature) may be interpreted as placing a lower limit of 2.5×10^{10} sec^{-1} ($\equiv 1.6\times10^{-5}$ eV) on the ICF rate in some substances containing Eu ions at configuration crossover.[17,18]

X-ray photoemission spectroscopy (XPS) of a $4f$ system at configuration crossover[19-21] is an example of a measurement in which the ICF rate is directly observable, in principle, as a linewidth. Such spectra contain resolved lines corresponding to transitions between definite manifolds of configuration-based single-ion states. The line with the highest-energy photoelectrons corresponds to a transition from the ICF manifold of $4f^n$ to that of $4f^{n-1}$, and its ideal width is of the order of the total ICF width $W = W^{(-)}_{n\to n-1} + W^{(+)}_{n-1\to n}$, although the lineshape is distorted by dynamic-screening effects.[22] This statement applies in both low-temperature and high-temperature regimes: since one is measuring the spectrum of one-electron excitations itself, rather than effects resulting from the thermal population of such excitations, ICF gives a broadening even in the zero-temperature limit. For other XPS lines corresponding to higher-energy ionic final states, the ICF rate $W^{(+)}$ must be replaced by a somewhat different expression reflecting the fact that such states have more mixing-decay channels available to them.[11] The linewidth resolution is presently limited to a few tenths of an eV by instrumental considerations, but with careful line-shape analysis[23] it may still be possible to establish nontrivial upper limits on $\Delta(\epsilon_F)$ from XPS measurements.

The above discussion for XPS applies essentially unchanged to all spectroscopic measurements in which one contemplates the resolution of various lines corresponding to transitions between different pairs of single-ion states or manifolds in an ICF system. Such lines are expected to be broadened by appropriate ICF or mixing-decay rates, and cannot be resolved unless their separation is larger than this broadening. Thus, for example, in $4f$ systems at configuration crossover one would not expect to find resolved crystal-field peaks in inelastic neutron scattering unless the ICF widths are unusually small, as in SmS.

Fermi-liquid theory[9] indicates that the magnetic susceptibility is influenced by interactions among the quasiparticles. In $4f$ systems at configuration crossover we would expect these interactions to be important (although certainly small compared to the intraionic Coulomb coupling U, since the quasiparticles represent well-correlated excitations). But we cannot calculate the interactions microscopically, and a phenomenological parametrization seems impractical since they would be expected to vary strongly from one case to the next depending upon the specific single-ion levels involved. Furthermore, $4f$ susceptibilities contain orbital-moment contributions which are usually larger than the spin-moment contributions,

and it is not clear how these could be inserted into Fermi-liquid theory. Quasiparticle concepts therefore do not seem useful in discussing the magnetic susceptibility. Instead, it seems better to base the discussion on the concept of lifetime-broadened configuration-based ionic levels.[2,3,24] The lifetime broadening which appears in such discussions has previously been identified with the nominal mixing width $\Delta(\epsilon_F)$, but the present discussion suggests that the total ICF width $(Q^{(-)}+Q^{(+)})\Delta(\epsilon_F)$ would be a better choice.

In view of the remarks made at the end of Sec. II, one must not think of the quasiparticle bands as maintaining a rigid shape when the 4f population is varied. Calculations based on the filling of such a rigid 4f band therefore do not appear to provide a reliable way of estimating the effect of finite mixing interactions on the equilibrium 4f population.[25]

V. CONCLUSIONS

We have discussed the spectra of 4f-like single-electron excitations in systems of 4f ions near configuration crossover. We have found that such 4f-like excitations give a strong, narrow resonance at the Fermi energy in the electronic density of states. The integrated density of this resonance is fixed by a sum rule and its width is identified with an interconfiguration fluctuation (ICF) rate for which semiquantitative estimates are available. We have discussed the physical interpretation of interconfiguration fluctuations, emphasizing that at low temperatures they correspond to a zero-point motion which is not always directly observable.

The quasiparticle spectrum which we have obtained has an obvious resemblance to a virtual-bound-state description.[26,27] However, the basic philosophy of our discussion is different from the usual virtual-bound-state approach since we regard the configuration-based ionic levels as being fundamental and derive the 4f-like quasiparticle bands from them.[4,25] The principal bands which we obtain in this way have widths and integrated densities different from those usually assumed in virtual-bound-state interpretations of such systems.

APPENDIX: EFFECTS OF INTRACONFIGURATIONAL SPLITTING

In this appendix we verify Eqs. (5) and (7), and evaluate the corresponding $Q^{(\pm)}$, for ICF manifolds containing the states within the LS or LSJ ionic ground levels. Our calculation is based upon the fact that the 4f creator $a^\dagger_{m\sigma}$ is a spherical double tensor of rank (l, s), which may be written in a more standard tensor notation as $(a^\dagger)^{ls}_{m\sigma}$. By the Wigner-Eckart theorem, a general matrix element of this operator between states within the LS ground terms of the two configurations may be written[10]

$$(n, LM_L SM_S\,|(a^\dagger)^{ls}_{m\sigma}|n-1, L'M'_L S'M'_S)$$
$$=(-1)^{L-M_L}(-1)^{S-M_S}\begin{pmatrix} L & l & L' \\ -M_L & m & M'_L\end{pmatrix}\begin{pmatrix} S & s & S' \\ -M_S & \sigma & M'_S\end{pmatrix}(n, LS\|(a^\dagger)^{ls}\|n-1, L'S')\,. \quad \text{(A1)}$$

The "stretched" states of the LS ground terms, i.e., the states with maximum M_L and M_S, are pure Slater determinants which can be built up for the successive configurations by successively adding 4f electrons of appropriate $m\sigma$. The matrix element on the left-hand side of Eq. (A1), taken between stretched states, and with $m=L-L'$, $\sigma=S-S'$, is therefore simply $+1$. This permits us to evaluate the reduced matrix element on the right-hand side of Eq. (A1) as

$$(n, LS\|(a^\dagger)^{ls}\|n-1, L'S')=\left[\begin{pmatrix} L & l & L' \\ -L & L-L' & L'\end{pmatrix}\begin{pmatrix} S & s & S' \\ -S & S-S' & S'\end{pmatrix}\right]^{-1}. \quad \text{(A2)}$$

When the ICF manifolds are identified with the LS ground terms, we use Eq. (A1) and the closure properties of the $3-j$ symbols[10] to obtain Eqs. (5) and (7), where

$$Q^{(-)}_{n\to n-1}=\left[\begin{pmatrix} L & l & L' \\ -L & L-L' & L'\end{pmatrix}^2\begin{pmatrix} S & s & S' \\ -S & S-S' & S'\end{pmatrix}^2(2L+1)(2S+1)\right]^{-1}, \quad \text{(A3)}$$

and where $Q^{(+)}_{n-1\to n}$ is given by the same expression with $(2L+1)(2S+1)$ replaced by $(2L'+1)(2S'+1)$.

When the ICF manifolds are identified with the LSJ ground levels, we use Wigner coefficients to decompose the 4f creator into parts of definite total angular momentum $j=\frac{5}{2},\frac{7}{2}$:

$$(a^\dagger)^{lsj}_\mu=\sum_{m\sigma}(a^\dagger)^{ls}_{m\sigma}(lm\,s\sigma\,|\,lsj\mu)\,. \quad \text{(A4)}$$

By a standard manipulation[10] the reduced matrix elements of these operators between LSJ states of the two configurations are found to be

$$(n, LSJ\|(a^\dagger)^{ls j}\|n-1, L'S'J') = (n, LS\|(a^\dagger)^{ls}\|n-1, L'S')[(2J+1)(2J'+1)(2j+1)]^{1/2} \begin{Bmatrix} L & L' & l \\ S & S' & s \\ J & J' & j \end{Bmatrix}. \tag{A5}$$

This leads again to Eqs. (5) and (7), where now

$$Q^{(-)}_{n\to n-1} = \left[\begin{pmatrix} L & l & L' \\ -L & L-L' & L' \end{pmatrix} \begin{pmatrix} S & s & S' \\ -S & S-S' & S' \end{pmatrix} \right]^{-2} \sum_j (2j+1)(2J'+1) \begin{Bmatrix} L & L' & l \\ S & S' & s \\ J & J' & j \end{Bmatrix}, \tag{A6}$$

and where $Q^{(+)}_{n-1\to n}$ is given by the same expression with $2J+1$ in place of $2J'+1$. In this version of Eqs. (5) and (7), $a^\dagger_{m\sigma}$ is replaced by $(a^\dagger)^{lsj}_\mu$ and the sum over m,σ is replaced by an equivalent sum over j, μ.

When the ICF manifolds are identified with CEF ground levels according to the weak-CEF scheme, we use a version of the irreducible-tensor method appropriate to the point symmetry of the CEF, based on 3-rep symbols defined analogously to the Wigner $3-j$ symbol.[28,29] Standard reduction coefficients are used to decompose the $4f$ creator of Eq. (24) into parts of definite symmetry classification according to the point group:

$$(a^\dagger)^{lsjd}_\delta = \sum_\mu (a^\dagger)^{lsj}_\mu (j\mu | jd\delta\rangle. \tag{A7}$$

Similar reduction coefficients give the amplitudes of the states of the CEF ground levels $|n, LSJb\beta\rangle$ and $|n-1, L'S'J'b'\beta'\rangle$ in terms of standard LSJ states. The general matrix element of the new $4f$ creator between states of the CEF ground levels can be written as a product of a 3-rep symbol and a reduced matrix element, where the latter is found to be

$$\langle n, LSJb\|(a^\dagger)^{lsjd}\|n-1, L'S'J'b'\rangle_p = \begin{bmatrix} J & j & J' \\ b & d & b' \end{bmatrix}_p (n, LSJ\|(a^\dagger)^{lsj}\|n-1, L'S'J'). \tag{A8}$$

Here the quantity in the square bracket is a reduction invariant defined and tabulated elsewhere.[28,29] Expressions corresponding to Eqs. (5) and (7) are again found to hold, where the $4f$ creator has the form (A7), the sum over m,σ is replaced by an equivalent sum over j, d, δ, and

$$Q^{(-)}_{n\to n-1} = \sum_{jdp} |\langle n, LSJb\|(a^\dagger)^{lsjd}\|n-1, L'S'J'b'\rangle_p|^2/[b], \tag{A9}$$

where $[b]$ is the degeneracy of the CEF ground level b of $4f^n$. $Q^{(+)}_{n-1\to n}$ is given by the same expression with $[b']$ in place of $[b]$.

The evaluation of CEF effects is particularly simple when the configuration $4f^n$ has a singlet LSJ ground level. Since the CEF has no effect on the singlet, $Q^{(+)}$ retains the same value as computed for ICF manifolds of LSJ type. As remarked following Eq. (18), $Q^{(-)}/Q^{(+)}$ equals the ratio of dimensionalities of the two ICF manifolds, so one needs only to know the degeneracy of the CEF ground level of $4f^{n-1}$ to find $Q^{(-)}$ and evaluate all the equations of Sec. III. A similar simplification applies when $4f^{n-1}$ has a singlet LSJ ground level. This simplified evaluation covers the examples discussed in the text, and indeed most examples arising in practice, since Ce, Sm, Eu, and Yb ions at configuration crossover all involve a configuration with a singlet LSJ ground level.

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