# Atomic mechanisms for the appearance of mixed valence states in lanthanides and actinides

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An investigation is reported of atomic mechanisms for the appearance of mixed valence states in rare-earth and actinide compounds due to the possibility of a transition of an electron belonging to a partly filled *f* shell from a state which has collapsed to weak localization. Self-consistent calculations of the corresponding atomic states are made by the Dirac–Fock method and the possibility of such transitions is demonstrated for a number of elements (Ce, Pr, Sm, Eu, Yb, U, Np). Arguments are given to show that this atomic effect, which is modified when such atoms form a condensed phase, can account for the appearance of a mixed valence and of heavy fermions in crystals. The important role of the electron–polaron effects associated in this case with relatively soft intraatomic excitations is pointed out.

## 1. INTRODUCTION

In recent years it has been suggested on several occasions that the orbital instability of the *f* shells, which is of purely atomic origin, may be responsible for a mixed valence[1,2] and heavy fermions[3] in intermetallic compounds based on lanthanides (Ce, Pr, Sm, Eu, Yb) and actinides (U, Np). It is well known[4–6] that in the case of atoms and ions with one electron in the 4*f* shell (Ce, La) or subshell (Eu) a slight change in the atomic potential results either in a strong compression of the wave function of an *f* electron (known as orbital collapse) or, conversely, expulsion of an *f* electron from an inner part of an atom to an outer Coulomb well of the effective potential (decollapse); in some cases there may be states distributed between two wells of the effective potential (Fig. 1).[6,7]

The degree of localization of an *f* electron in the inner core part of an atom with characteristic size $r_{\text{in}} \sim 1$ a.u. or in its outer part at radii $r_{\text{out}} \sim -$ 3–20 a.u. determines in principle the valence of an atom in a crystal. Since a mixed valence and heavy fermions are observed in intermetallic compounds of precisely those elements which exhibit a characteristic orbital instability, it is natural to relate these properties. The first step is to determine the characteristic features of the behavior of free atoms with partly filled *f* shells which can give rise to a mixed valence and heavy fermions in crystalline compounds. We shall analyze possible mechanisms for the influence of an orbital instability of free atoms on an instability of the valence of the *f* elements in the crystalline environment and we shall give the results of numerical calculations of excited states of free atoms exhibiting such an instability.

## 2. WHAT IS A MIXED VALENCE OF A FREE ATOM?

In the generally accepted scheme for filling the atomic shells we can always identify a configuration corresponding to the minimum total energy of an atom. For example, in the lanthanide series the standard ground-state configuration is $[\mathrm{Xe}]4f^n 6s^2$ [the exceptions to this rule are Ce$(4f^7 5d^1 6s^2$ and Gd$(4f^7 5d^1)6s^2)$]. In the case of light actinides (Pa–Bk) the lowest term usually corresponds to the $[\mathrm{Rn}]5f^n 6d^1 7s^2$ configuration and only Pu and Am have the ground-state configuration $5f^{n+1} 7s^2$.

It is known from Ref. 5 that the 4*f* electrons in atoms characterized by $Z > 58$ and the 5*f* electrons in atoms with $Z > 91$ are localized within the filled shells of the core: $\bar r_f < \bar r_{[\mathrm{Xe}]}, \bar r_{[\mathrm{Rn}]}$. If the valence of a free atom is understood to be its reactivity, governed by the number of electrons in the outer orbitals with an average radius $\bar r > \bar r_{[\mathrm{Xe}]}, \bar r_{[\mathrm{Rn}]}$, then all the *d* and *s* electrons are valence electrons so that a free atom of an actinide or a lanthanide should have valence 2 or 3. If we adopt this definition, we can speak of a mixed valence of a free atom only when an *f* electron is delocalized under the influence of some perturbation or, conversely, if a *d* electron partly collapses and goes over to an *f* state localized within the core. A convenient measure of the degree of localization of *f* electrons is the quantity

$$n_f = \int_0^{r_0} |g_f(r)|^2 r^2\, dr, \tag{1}$$

where $g_f(r)$ is the radial part of the wave function of an *f* electron and the radius $r_0$ is arbitrarily chosen to be that value which is given by

$$\int_0^{r_0} |g_f^{(0)}(r)|^2 r^2\, dr = 0.9 \tag{2}$$

for the wave function of an *f* electron in the ground state of a given atom. This definition is based on the use of the existing experimental static (as well as quasistatic) methods of finding the valence, interpolations based on either determination of the effective radius of the core (interpolation of the specific volumes) or determination of the density of the core electrons (interpolation of the isomeric shift of Mössbauer spectra or the chemical shifts of x-ray lines).

The mechanisms which can give rise to a mixed valence are usually an admixture to the ground-state configuration (for example, $f^n ds^2$) of low-lying excited terms ($f^{n-1} d^2 s^2$ or $f^{n+1} s^2$)[8] or the orbital instability of the *f* shell mentioned above.[2,3] In strongly excited states of atoms and ions formed as a result of transitions of electrons from the inner x-ray shells to the outer shells we find that the dynamic polarization effects may defy the one-electron nomenclature of the atomic states.[9] We shall consider the atomic properties of the elements Ce, Pr, Sm, Eu, Yb, U, and Np which may exhibit these mechanisms. The results reported below were

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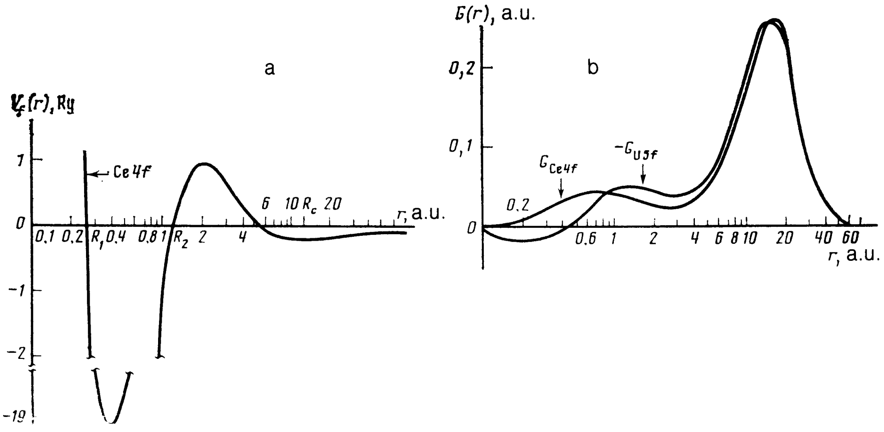

FIG. 1. a) Effective potential $V_f(r)$ of the $f$ electrons in Ce. b) Major components of $G(r)$ in the case of partly decollapsed wave functions of the $f$ electrons of Ce and U ($G_{5f}$ is represented with the reversed sign).

obtained by numerical calculations carried out using the Dirac–Fock method with full allowance for the exchange.[10,11]

### 3. MIXING OF ATOMIC CONFIGURATIONS

The possibility of describing the states of atoms by fractional occupation numbers of atomic orbitals, which appear as a result of mixing of states with closely spaced terms belonging to different atomic configurations, was considered by Slater *et al.*[12] specifically in the case of the $3d^n 4s^2$ states of transition metals belonging to the iron group. These states may have an admixture from the $3d^{n+1}4s$ state with a lower excitation energy. In the standard task of calculation of the atomic terms it is meaningful to consider only occupation numbers of the ground state which are integers. The possibility of mixing is due to external perturbations. In the later stages of the analysis it is important that the degree of mixing be governed not only by the external field, but also by the Coulomb and exchange interactions of electrons at hybridized orbitals, because in the self-consistent procedure for calculation the energy terms the nature of the wave functions depends on the configuration and the basis which diagonalizes the states for the $d^n s^2$ configuration is not the basis for the $d^{n+1}s$ configuration. Therefore, the possibility of a change in the atomic configurations under the influence of external forces may be accompanied by a departure from the one-electron nomenclature of the terms.[9,12] This means that the Hamiltonian of the system described in the basis of functions with a fixed configuration,

$$H=\sum_{i=d,s}\varepsilon_i a_{i\sigma}^+a_{i\sigma}+\sum_{ij}\sum_{\sigma\sigma'}(i\sigma,j\sigma'|Q|i\sigma,j\sigma')\cdot a_{i\sigma}^+a_{j\sigma'}^+a_{j\sigma'}a_{i\sigma}+\sum_{ij}\sum_{\sigma\sigma'}(i\sigma,j\sigma'|Q|j\sigma,i\sigma')a_{i\sigma}^+a_{j\sigma'}^+a_{i\sigma'}a_{j\sigma}, \quad (3)$$

may contain off-diagonal exciton averages of the $\langle a_d^+ a_s\rangle$ type[2,13] as a result of interconfiguration transitions induced by an external perturbation.

The Coulomb mixing idea has been used to explain the mixed-valence phenomenon even in the early stages of investigating this effect. For example, it is shown in Ref. 14 that in the case of Ce we can expect mixing of the atomic configurations $4f^1 5d^1 6s^2$ and $4f^0 5d^2 6s^2$ under pressure (which simulates a change in the radius of a Wigner–Seitz cell). The gap between the initial equilibrium atomic terms in Ce is $\Delta E_{fd}=0.4$ eV, but inclusion (in the self-consistent atomic calculations) of mixed configurations of the $4f^x 5d^{2-x} 6s^2$ type, allowing for the $x$-dependent modification of the wave functions, gives the absolute minimum of the total energy of an atom when $0.4<x<0.5$. This calculation naturally does not provide a full explanation of the mixed valence of metallic cerium, but it is evidence of an internal property of this element that aids the appearance of a mixed valence.

Figure 2 gives the results of a Dirac–Fock calculation for a free atom of Yb, which is a hole analog of Ce, in which the competing configurations are $4f_{5/2}^6 4f_{7/2}^7 5d_{3/2}^1 6s^2$ and $4f_{5/2}^6 4f_{7/2}^8 6s^2$, the latter separated from the former by 0.17 eV. The minimum of the total energy of the mixed configuration $4f_{5/2}^6 4f_{7/2}^{8-x} 5d^x 6s^2$ occurs at $x\approx 0.55$.

The fundamental role of the Coulomb interaction in this mechanism can also be demonstrated using an elementary model of an atom with two configurations close on the energy scale when one of them represents a localized state of an electron of energy $\varepsilon_0$ and the other a delocalized electron corresponding in the sense described above to a state $\varepsilon_1$ (Ref. 3). The Hamiltonian of such a system derived allowing only for the Coulomb interaction can be used in its simplified form

$$H=\varepsilon_0\sum_\beta f_\beta^+f_\beta+\varepsilon_1\sum_\alpha b_\alpha^+b_\alpha+U_{ff}\sum_{\beta\beta'}f_\beta^+f_\beta f_{\beta'}^+f_{\beta'}+U_{fb}\sum_{\alpha\beta}f_\beta^+f_\beta b_\alpha^+b_\alpha. \quad (4)$$

Here $f_\beta$ and $b_\alpha$ are the second-quantization operators for

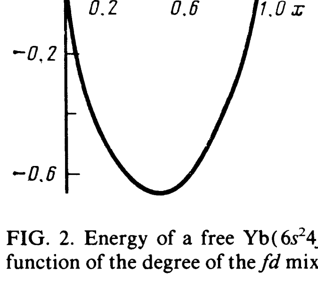

FIG. 2. Energy of a free Yb($6s^2 4f_{5/2}^6 4f_{7/2}^{7+x} 5d_{3/2}^{1-x}$) atom plotted as a function of the degree of the $fd$ mixing.

collapsed and delocalized states, respectively; $\beta$ and $\alpha$ are the quantum numbers of electrons. The Hamiltonian includes only the strongest interactions between collapsed electrons in one shell and the Coulomb interaction between electrons in different shells (interactions of Hubbard and Falicov in the terminology adopted in the theory of mixed valence). Physically, it is clear that we have $\Delta\varepsilon_{10} = \varepsilon_1 - \varepsilon_0 > 0$, $U_{ff} > U_{fb}$.

We shall assume that the Hamiltonian (4) is written down in terms of the second-quantization operators for a fixed number $n$ of electrons in the $f$ shell. Adding another electron to the system, we can locate it at the lower level $\varepsilon_0$, but because the electrons in the collapsed state interact strongly it may be preferable from the energy point of view for partial delocalization to occur; in the course of this process a reduction in the one-electron energy $\Delta\varepsilon_{10}$ is balanced by an increase in the interaction energy. In accordance with the concept of transition states,[12] we shall seek the wave function of a system with $n + 1$ electrons in the form of an antisymmetric product of one-electron wave functions of the type

$$|\Psi)=\sin\theta|f)+\cos\theta|b), \tag{5}$$

where $\theta(n_f)$ is a variational parameter depending on the total number of electrons in the collapsed state

$$n_f=\sum_\beta f_\beta{}^+ f_\beta.$$

It is interesting to note that a mixed configuration appears even in the simplest model postulating that $U_{fb} = 0$, which is entirely due to the Hubbard repulsion. Assuming that the degree of degeneracy of the $f$ levels is high, we find the energy of the ground state for this case:

$$E(n_f)=(\Psi|H|\Psi)=\varepsilon_0\nu_f+\varepsilon_1(n_f-\nu_f)+\frac{\nu_f{}^2}{n_f{}^2}\frac{n_f(n_f-1)}{2}U_{ff}. \tag{6}$$

Here, we have introduced $\nu_f = n_f \sin^2\theta$ for the number of collapsed electrons in the mixed configuration. Minimization of the energy with respect to $\nu_f$ gives

$$\nu_f=n_f\Delta\varepsilon_{10}/(n_f-1)U_{ff}. \tag{7}$$

If in the initial configuration we have $\nu_f(n_f) = n_f = n$, we find from Eq. (7) that

$$\Delta\varepsilon_{10}/U_{ff}=n_f-1, \tag{8}$$

so that for a system with an excess electron we obtain

$$\nu_f(n+1)=(n_f+1)\Delta\varepsilon_{10}/n_fU_{ff}=n-n^{-1}<n. \tag{9}$$

If the level $\varepsilon_0$ lies deeper than deduced from Eq. (8), $\nu_f$ for the modified configuration is greater than in Eq. (9) and in general its value may be within the interval

$$n-n^{-1}<\nu_f(n+1)<n+1. \tag{10}$$

This very simple model shows that conditions may be realized in an atom when the addition of an excess electron results in an effective reduction in the electron density in the core region (rather than an increase) because of modification of all the electron states which accompanies an increase in the number of electrons in the outer shells.

If we allow for the interaction between collapsed and delocalized electrons $U_{fb}$, we find that Eq. (7) becomes

$$\nu_f=\frac{n_f}{1-n_f}\frac{\Delta\varepsilon_{10}-U_{fb}(n_f-1)}{U_{ff}-2U_{fb}}, \tag{11}$$

but the integral of possible changes in the valence described by Eq. (10) is affected little.

## 4. PARTLY DECOLLAPSED STATES

In this section we shall consider the mechanisms of destabilization of the valence of lanthanides and actinides associated with the orbital instability of the $4f$ and $5f$ shells themselves. As mentioned in the Introduction, this instability is due to the two-well nature of the effective potential for the $f$ electrons (Fig. 1a), because of which we can expect the appearance of hybrid states of the $f$ electrons. Such partly decollapsed states, which in terms of our study can be regarded as mixed valence states of free atoms, were found in the form of excited states of Ba I and Ba II atoms and ions (see, for example, the review given in Ref. 15). In a neutral Ba atom an $f$ electron in an excited $4f6s$ state is localized in the outer Coulomb well of the potential $V_f(r)$. However, calculations and experiments show[7,15] that in the case of the Ba II ion ($4d^9\,4\tilde{f}$) an electron transferred from an inner to the valence $4f$ shell due to the absorption of an x-ray photon is in a partly decollapsed state and is distributed between the two wells of the potential $V_f(r)$. In the case of the Ba I atom ($4f^9 4\tilde{f}6s$) an $f$ electron is in a virtual level near the edge of the continuum, in resonance with a state $\varepsilon_f$ in the continuous spectrum, but with atomlike behavior of the $4f$ wave function in the range $r < 1$ a.u..

Theoretical work[6] has established that excited states of this type are exhibited by neutral La($4\tilde{f}^1_{5/2}6s^2$) and Eu($4f^6_{5/2}4\tilde{f}^1_{7/2}6s^2$) states. The mechanism of formation of a hybrid state was investigated by continuous deformation of the atomic potential $V_f(r)$, selected in the form

$$V_f(r)=-\frac{2Z}{r}\varphi_{base}\left[r\left(\frac{Z}{Z_{base}}\right)^{1/3}\right]+\frac{l(l+1)}{r^2} \tag{12}$$

(in atomic units). The potential was deformed by formal variation of the value of $Z$ away from $Z_{\text{base}}$, equal to 58 and 64 for La and Eu, respectively. In narrow intervals $56.35 < Z < 56.50$ for La and $62.53 < Z < 62.61$ for Eu the $\tilde{f}$ wave functions are also distributed between the two wells of the potential of Eq. (12). It was pointed out that the possibility of localizing an $f$ electron in the inner part of an atom (inner well of the effective potential) is closely related to the power of a potential well defined by

$$W=\int_{R_1}^{R_2}[V_f(r)+2E]r\,dr, \tag{13}$$

which in its turn is governed by the electron configuration of an atom. Here, $E$ is the binding energy of an $f$ electron, whereas $R_1$ and $R_2$ are the turning points for $E = 0$ (Fig. 1a). For each atom there is a certain minimum value $W_c$, such that if $W > W_c$ an electron is in a collapsed state. Consequently, for $W$ less than a certain value $W_b$ an electron is outside the volume of an atom so that the power of the inner well describes uniquely the valence of a given atom.

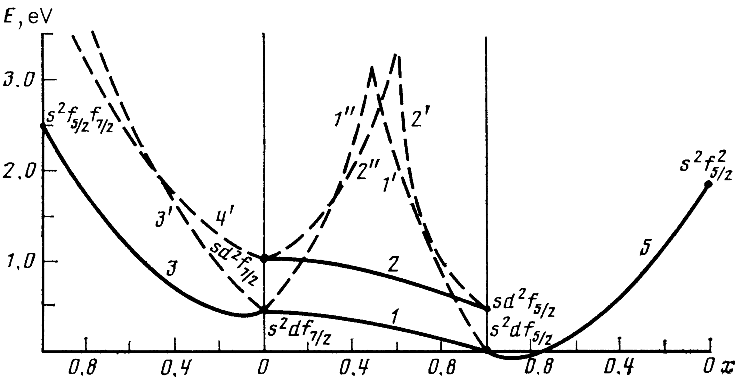

FIG. 3. Energy $E$ (in electron volts) of a Ce atom in mixed configurations: 1) $s^2d_{3/2}f^{1-x}_{7/2}f^x_{5/2}$; 1') $s^2d_{3/2}\tilde f^{1-x}_{7/2}f^x_{5/2}$; 1'') $s^2d_{3/2}f^{1-x}_{7/2}\tilde f^x_{5/2}$; 2) $sd^2_{3/2}f^{1-x}_{7/2}f^x_{5/2}$; 2') $sd^2_{3/2}\tilde f^{1-x}_{7/2}f^x_{5/2}$; 2'') $sd^2_{3/2}f^{1-x}_{7/2}\tilde f^x_{5/2}$; 3) $s^2d^{1-x}_{3/2}f^x_{5/2}f_{7/2}$; 3') $s^2d^{1-x}_{3/2}\tilde f^x_{5/2}f_{7/2}$; 4') $sd^{2-x}_{3/2}\tilde f^x_{5/2}f_{7/2}$; 5) $s^2d^x_{3/2}f^{2-x}_{5/2}$. In Figs. 3–6 the continuous curves represent the configurations with collapsed-state electrons, whereas the dashed curves represent the configurations with partly decollapsed electrons.

Of special interest to us is the circumstance that the excitation energy of the Coulomb states in the outer well of a potential is small: $\Delta E_{f\tilde f} = 2.0$ eV for La and 2.8 eV for Eu. In some cases it is found that $\Delta E_{f\tilde f}$ is comparable with the energy of $fd$ transitions $\Delta E_{fd}$, which encouraged us to extend the basis in calculations of mixed configurations using the Slater method[12] and to include in the set of trial functions the decollapsed $\tilde f$ states, in addition to the $f$ and $d$ states. As in Ref. 6, the $f$ electron wave functions were calculated in the $jj$-coupling approximation, so that electrons were distributed between subshells with momenta $j = 5/2$ and $7/2$. The variational basis for an atom with $N$ electrons in the outer $sdf$ shells included $(sd)^3(f^x_{j_1}f^{N-3-x}_{j_2})$ configurations with a fixed number of the $sd$ electrons and mixed $f$ configurations, when partial decollapse of an electron occurs in one of the $f_j$ subshells, as well as states of the type $(sd)^{3-x}f^x_{j_1}f^{N-3}_{j_2}$, when an electron from an outer $sd$ shell is transferred partly to an $f$ shell, where it can be in collapsed or decollapsed states.

Figure 3 gives the results of calculations carried out for a neutral atom of Ce. Its ground state is $s^2df_{5/2}$ (for simplicity, we shall omit the principal quantum numbers). The lowest excited state $s^2df_{7/2}$ is separated from the ground state by a gap $\Delta E_{ff} = 0.42$ eV. Mixed Slater states $s^2df^x_{5/2}f^{1-x}_{7/2}$ form branch 1 of the total energy of an atom. There is also a second solution (branches 1' and 1'') when the same $f$ electrons, the fraction of which in the mixed configuration is $< 0.5$, is transferred to a Coulomb well with a binding energy $\varepsilon_{\tilde f} = 0.86$ eV and with an average radius $\langle r \rangle = 17.5$ a.u. In the determination of the valence of an atom and other physical properties it is important that an inner well retain an electron density "tail" (Fig. 1), so that our decollapsed states are of the same type as the solutions found earlier for Ba ions and La and Eu atoms in Refs. 6 and 7, and in determining the valence of, for example, the $s^2d\tilde f^{0.5}_{5/2}f^{0.5}_{7/2}$ configuration corresponding to a large component of the radial wave function $G(r) = rg(r)$ shown in Fig. 1a, we find that the application of the criteria of Eqs. (1) and (2) gives not 3.5 but a somewhat smaller result. Similar solutions are also obtained for excited configurations of the $sd^2f^x_{5/2}f^{1-x}_{7/2}$ type (curves 2, 2', and 2'' in Fig. 3).

An additional solution with a decollapsed $\tilde f$ electron appears for a mixed configuration of the $s^2d^{1-x}\tilde f^x_{5/2}f_{7/2}$ type, when one of the outer $d$ electrons is transferred to an $f$ orbit (curve 3'). For these configurations there is also a second solution with a lower total energy, corresponding to collapsed electrons in both subshells (curve 3). In the case of states based on the $sd^2$ configuration we also obtain a decollapsed state solution similar to the branch 3' (curve 4').

It should however be pointed out that we do not obtain metastable states of the Ce atom with an $\tilde f$ electron distributed between two wells of $V_f(r)$, the existence of which is postulated by the Schlüter–Varma model.[2] In this sense our results are close to those of Bringer[16] who obtained a monotonic increase in the total energy as a result of transfer of the $f$ electron density from the inner to the Coulomb well. Such minima are more likely to occur for the states representing mixing of the $f$ and $d$ functions (curve 5 in Fig. 3) and the absolute minimum of the energy of a free atom corresponds to the $s^2d^x_{3/2}f^{2-x}_{5/2}$ configuration with the number of $f$ electrons exceeding unity.

The properties of Ce are close to those of an atom of Pr for which the ground configuration is, according to our calculations, $s^2d_{3/2}f^2_{5/2}$ (Fig. 4). In this case the spin–orbit interaction is twice as large as for Ce, $\Delta E_{ff} = 0.87$ eV, and

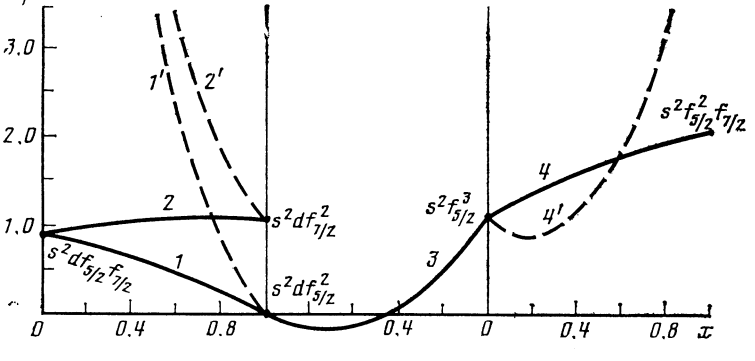

FIG. 4. Energy of a Pr atom in mixed configurations: 1) $s^2d_{3/2}f^{1+x}_{5/2}f^{1-x}_{7/2}$; 1') $s^2df^{1+x}_{5/2}\tilde f^x_{7/2}$; 2) $s^2d_{3/2}f^{1-x}_{5/2}f^{1+x}_{7/2}$; 2') $s^2d_{3/2}\tilde f^{1-x}_{5/2}f^{1+x}_{7/2}$; 3) $s^2d^x_{3/2}f^{3-x}_{5/2}$; 4) $s^2f^{3-x}_{5/2}f^x_{7/2}$; 4') $s^2f^{3-x}_{5/2}\tilde f^x_{7/2}$.

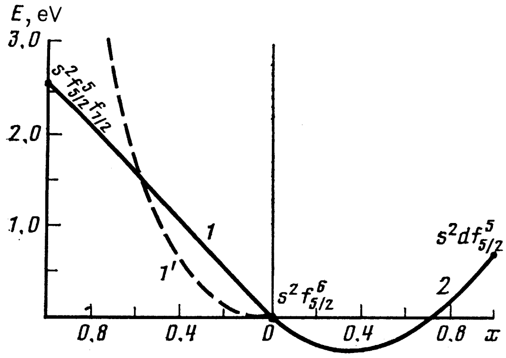

FIG. 5. Energy of an Sm atom in mixed configurations: 1) $s^2f^{6-x}_{5/2}f^x_{7/2}$; 1') $s^2f^{6-x}_{5/2}\tilde{f}^x_{7/2}$; 2) $s^2f^{6-x}_{5/2}d^x_{3/2}$.

decollapsed state branches appear for mixed configurations of the types $s^2d\tilde{f}^{1+x}_{5/2}f^{1-x}_{7/2}$ (branch 1'), $s^2d\tilde{f}^{1-x}_{5/2}f^{1+x}_{7/2}$ (branch 2'), and $s^2f^{3-x}_{5/2}\tilde{f}^x_{7/2}$ (branch 4'). In the first two cases these branches lie higher on the energy scale than the normal collapsed state branches 1 and 2, whereas the decollapsed state 4' corresponding to low values of $x$ lies below the collapsed state branch 4. As in the case of Ce, an absolute minimum of the energy corresponds to a mixed state with three electrons distributed between the $d_{3/2}$ and $f_{5/2}$ shells (curve 3).

The situation is slightly different in the case of a nominally divalent atom of Sm, which has the $s^2f^6_{5/2}$ configuration in the ground state. In the case of this atom there are again two branches of mixed states $s^2f^{6-x}_{5/2}f^x_{7/2}$ (Fig. 5): a decollapsed state branch 1' with an $\tilde{f}_{7/2}$ electron in a Coulomb well at low values of $x$ lies below a collapsed state branch 1 and competes with the "standard" mixed valence state $s^2d^x_{3/2}f^{6-x}_{5/2}$ (branch 2).

As pointed out already, the power of the inner well plays a decisive role in the appearance of decollapsed states. For all the rare-earth elements under discussion we have $W_{\text{in}} > 2.1$ for collapsed states and $W_{\text{in}} < 1.9$ for decollapsed states. The depth of the $f$ level in a collapsed state depends strongly on the configuration, but usually exceeds 8 eV. For a decollapsed state it is practically constant, $\varepsilon_{\tilde{f}} = 0.85$–$0.86$ eV, and it corresponds to the Coulomb energy of an $f$ electron for all the investigated atoms.

There is a considerable interest in the pattern of the spectrum of excitations of an atom of U, which forms a large number of compounds with a mixed valence and heavy fermions; these are intermetallic compounds with elements of the IB, II, III, and VIII groups (Ref. 17). In the ground state an atom of U has the $7s^26d_{3/2}5f^3_{5/2}$ configuration. Figure 6 shows the energy of an atom of U for a number of mixed configurations. In the case of U, as in the case of the rare-earth elements discussed above, there are states with mixed $f$ shells for a fixed number of the $sd$ electrons: collapsed and decollapsed state branches with the configurations $s^2df^{3-x}_{5/2}f^x_{7/2}$ (curves 1 and 1') and $sd^2f^{3-x}_{5/2}f^x_{7/2}$ (curves 2 and 2'). In the case of states characterized by the transfer of a $d$ electron to the $f$ shell ($s^2d^{1-x}f^3_{5/2}f^x_{7/2}$ configuration) a characteristic feature is that an energy branch 3' for a decollapsed state at low values of $x$ lies below a collapsed state branch 3.

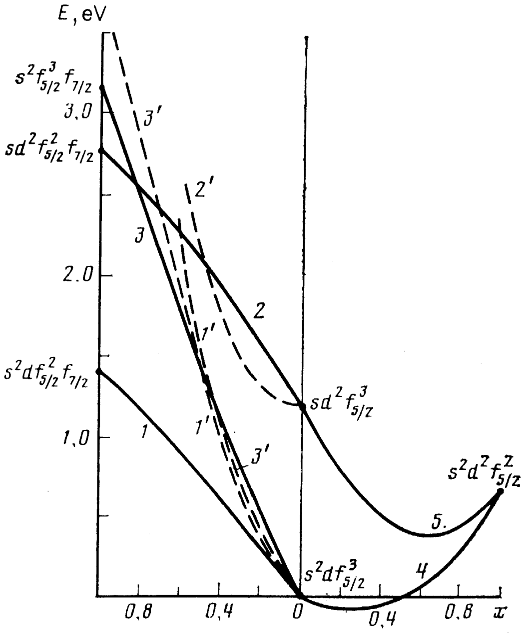

FIG. 6. Energy of a U atom in mixed configurations: 1) $s^2d_{3/2}f^{3-x}_{5/2}f^x_{7/2}$; 1') $s^2d_{3/2}f^{3-x}_{5/2}\tilde{f}^x_{7/2}$; 2) $sd^2_{3/2}f^{3-x}_{5/2}f^x_{7/2}$; 2') $sd^2_{3/2}f^{3-x}_{5/2}\tilde{f}^x_{7/2}$; 3) $s^2d^{1-x}f^3_{5/2}f^x_{7/2}$; 3') $s^2d^{1-x}f^3_{5/2}\tilde{f}^x_{7/2}$; 4) $s^2d^{1+x}f^{3-x}_{5/2}$; 5) $s^{1+x}d^2f^{3-x}_{5/2}$.

It should be pointed out that a state with four electrons in the $f$ shell is closer to an instability threshold, as suggested in Ref. 3: in a collapsed-state configuration $s^2f^3_{5/2}f_{7/2}$ the level $f_{7/2}$ is anomalously shallow, $\varepsilon_f = 4.48$ eV, whereas in a corresponding decollapsed state with an energy $E = 4.08$ eV the wave function of an $\tilde{f}$ electron is of hybrid nature with a large fraction of the charge in an inner well (Fig. 1b).

An absolute energy minimum lies on a branch 4 and corresponds to an $s^2d^{1.25}_{3/2}f^{2.75}_{5/2}$ configuration. An overall characteristic of U is that the energies of the decollapsed- and collapsed-state branches for the same configuration are similar (they differ by less than 0.25 eV). Zero-gap branches 1, 1', 3, and 3' almost merge at these values of $x$ giving rise to a high density of levels for mixed configurations.

Two types of $f$ states have been reported also for an atom of Np in the mixed configurations $7s^26d_{3/2}5f^{4-x}_{5/2}5f^x_{7/2}$ and $7s6d^2_{3/2}5f^{4-x}_{5/2}5f^x_{7/2}$. The situation is similar to that in the case of U. The threshold separating an excited state $sd^2f^4_{5/2}$ from the ground state $s^2df^4_{5/2}$ amounts to 1.23 eV in the case of Np. The power of the inner well in actinides is less than 9.5 for decollapsed states and 9.8 for collapsed states.

Our examination of a large group of lanthanides and actinides thus shows that an electron which begins filling of the $f$ shell or subshell with a given total momentum $j$ may be in two states: a collapsed state within the atomic core and a partly decollapsed state distributed between the inner and outer wells of the effective potential $V_f(r)$ so that a considerable fraction of the $f$ electron density is displaced to the peripheral (outer) region of the valence shells and only a small part remains within the core. Decollapsed states of the type shown in Fig. 1, together with the mixed $f^{n-x}d^x$ configuration studied earlier, can be found if they are regarded as the valence states of free atoms. Decollapsed states of isolated atoms are excited, but in a solid the situation may change significantly.

## 5. ORBITALLY UNSTABLE ATOMS IN A CRYSTAL ENVIRONMENT

When a free atom becomes part of a crystal lattice the self-consistent potential experienced by electrons in the valence shell may change considerably, the participation of the valence electrons in the formation of chemical bonds may become important in a crystal, and finally we may find that the dynamic interaction between intraatomic excitations in partly filled shells and the continuum of electron–hole excitations near the Fermi level is important in a metal or a semiconductor because this interaction is responsible for the itinerant (collective) state of a system consisting of the *df* electrons in a partly filled shell and the continuum of conduction electrons where the *d*- and *f*-electron states differ greatly from the Dirac–Fock one-electron states of free atoms. In this section we shall consider the role of soft excitations accompanied by a change in the configuration (investigated in the preceding section) in the realization of all these mechanisms.

The simplest method of allowing for the role of the crystal environment involves replacement of the atomic boundary conditions with the Wigner–Seitz conditions:

$$\begin{aligned} dg(r)/dr|_{r=R_{WS}}&=0 \quad \text{for even} \quad l,\\ g(r)|_{r=R_{WS}}&=0 \quad \text{for odd} \quad l. \end{aligned} \tag{14}$$

Here, $R_{WS}$ is the Wigner–Seitz radius in a crystal. We checked the influence of a change in the boundary conditions on the collapsed states by ensuring complete self-consistency of atoms on the basis of the Dirac–Fock method using the boundary conditions of Eq. (14) and we calculated the strength of the inner well of the effective self-consistent potential $V_f(r)$, which—as mentioned already—determines uniquely the degree of localization of the *f* electrons. It was found that the strength $W$ of the well for a Wigner–Seitz atom differs by no more than a fraction of a percent from $W$ for a free atom. For example, in the case of Ce in the ground state it is found that a free atom is characterized by $W_{\text{free}} = 2.096$, whereas a Wigner–Seitz atom with a radius $R_{WS} = 5$ a.u. is characterized by $W_{\text{cell}} = 2.093$. If $R_{WS} = 3.5$ a.u., we have $W_{\text{cell}} = 2.087$. For U in the ground state we find that $W_{\text{free}} = 9.784$, whereas for a Wigner–Seitz atom with a radius $R_{WS} = 5$ a.u., we find that $W_{\text{free}} = 9.746$. Such changes are insufficient to displace an *f* electron from the inner well of the potential $V_f(r)$. Redistribution of the valence electrons due to binding of rare-earth ions to form a crystal may be more important.

The electrons in the outer valence shells are largely in the itinerant (collective) state in a crystal so that instead of a neutral atom we have to consider a charged *f* ion in the screening field of the conduction electrons. Self-consistent numerical calculations have not yet been carried out for systems of this kind. In a recent investigation[18] the $UBe_{13}$ system was modeled by a $U^{4+}$ ion immersed in a homogeneous electron gas considered in the jellium model. However, the approximation of a local density functional used to describe the exchange-correlation contribution to $V_f(r)$ is far too rough to account for the effects of interest to us, because the nonlocal exchange potential plays a decisive role in the formation of the *f* states distributed between the two wells.[6,19]

In view of the complexity of the numerical description of the nonlocal exchange for the *f* atoms in the crystal lattice, we shall confine ourselves to quantitative considerations of possible changes in the spectrum of low-lying elementary excitations of these atoms. We shall continue to use the Wigner–Seitz model and represent the total energy of a crystal as a sum of the energies $E = NE_{WS}$ of pseudoatoms in which the valence electrons are all those that contribute to the cohesive energy of a metal, defined as the difference

$$E_{coh}=E_{WS}\{f_{\text{CS}}^{n-x}b^{3+x}\}-E_{at}\{f_{\text{CS}}^{n}(ds)^{3}\}, \tag{15}$$

whereas the core electrons will be those *f* electrons that remain in a collapsed state $f_{\text{CS}}$. The number of electrons that remain in the core and are used in binding now no longer has to be an integer[12] and the value of $x$ can be found by minimizing the total energy of a pseudoatom in the same way as was done for a free atom in the preceding section. Equation (15) provides the necessary corrections in the case of compounds of Sm and Eu characterized by a base valence of 2.

The valence states are not only the *ds* states, as in the usual theory of rare-earth metals, but also decollapsed states $\tilde{f}_{\text{DS}}$. The Wigner–Seitz radius of rare-earth compounds and actinides is such that the region of the outer well of the potential $V_f(r)$ is outside $R_{WS}$, although it is possible that in the case of a self-consistent state in a crystal the radius of the outer well may be considerably less than the Coulomb radius of a neutral free atom. In particular, it is clear that this radius decreases strongly in the transition from a neutral atom to an ion. In the case of a singly ionized atom, for example, the distance $R_c$ (Fig. 1a) decreases by a factor of two (see also Ref. 19). Figure 7 shows schematically the potential relief of the *f* electrons in compounds for which there is no direct overlap between the *f* atoms and for which the region between them is occupied by the normal component of an intermetallic compound, a chalcogenide, or a pnictide with a relatively smooth potential (or pseudopotential) relief (shaded region *B* in Fig. 7). Since the *f* wave function in a decollapsed state is distributed between both wells of the potential $V_f(r)$ (Fig. 1b), when the atomic potentials overlap the outer part of the *f* wave becomes hybridized with the corresponding states in the band continuum, whereas the inner part ensures retention of a virtual state under a centrifugal barrier with a characteristic width $\Gamma_f$ similar to the virtual states in transition metals responsible for the formation of the *d* energy bands.[20] The atomic 5*d* and 6*d* levels of lanthanides and actinides in a crystal are also converted to

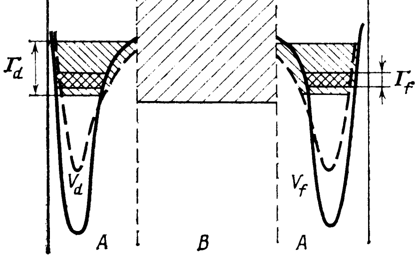

FIG. 7. Potential relief and schematic representation of the energy levels of intermetallic compounds of rare-earth elements: *A* is the region occupied by a rare-earth atom and *B* is the region of the band electrons; $R_{WS}$ is the approximate value of the Wigner–Seitz radius for the cell of the rare-earth atom.

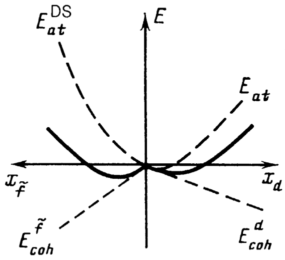

FIG. 8. Energy of a pseudoatom in a Wigner–Seitz cell (continuous curves) and its components $E_{\mathrm{at}}$ and $E_{\mathrm{coh}}$ (dashed curves) in the case of $f^{n-x}\tilde{f}^x$ (on the left) and $f^{n-x}d^x$ (on the right) mixing.

virtual states, but their widths obey $\Gamma_d > \Gamma_f$ and clearly in many cases we can expect a direct overlap of the $d$ states located at different sites.

In view of the direct or indirect overlap, the levels $\varepsilon_f$ and $\varepsilon_d$ are smeared out into energy bands and if these bands lie in the region of the Fermi level $E_F$, i.e., if $|E_F - \varepsilon_{\tilde{f}(d)}| < \Gamma_{\tilde{f}(d)}$, the total energy of a pseudoatom decreases and the improvement in the energy because of delocalization of the $\tilde{f}$ and $d$ electrons determines the cohesive energy $E_{\mathrm{coh}}$ of Eq. (15). When the number of the $\tilde{f}$ and $d$ electrons remaining under the Fermi level is small, the corresponding contributions to the cohesive energy can be regarded as linear functions of $x_f$ and $x_d$ (see, for example, Ref. 21):

$$E_{\mathrm{coh}} \approx -(\alpha_d x_d + \alpha_f x_f). \tag{16}$$

The coefficients $\alpha_d$ and $\alpha_f$ can be estimated knowing the contributions of the $d$ and $f$ electrons to the cohesive energy of the pure $4f$ and $5f$ metals. For example, in the case of light actinides if we use the Fourier estimates of the sublimation energy,[22] we can assume that $\alpha_f \approx 2\alpha_d \approx 4$ eV. Then, adding the cohesive energy $E_{\mathrm{coh}}$ of Eq. (16) to the energy $E_{\mathrm{at}}$ for various configurations calculated in the preceding section, and minimizing $E_{\mathrm{WS}}$ of Eq. (15) with respect to $x_d$ and $x_f$, we can obtain the behavior shown schematically in Fig. 8. Depending on which of the two minima of the total energy is lower, our Wigner–Seitz crystal exhibits a mixed valence state with the predominant $f\tilde{f}$ or $fd$ mixing. It should be remembered that in the crystal state the $s^2d$-type configurations of the outer electrons are frequently replaced with mixed $s^{2-x}d^{1+x}$ configurations close to $sd^2$. For example, in the case of heavy fermions in the compound UPt$_3$ the band calculations give $n_d = 1.44$ and $n_{s+p} = 0.72$ for the partial occupation numbers in the U sublattice.[23] Therefore, the gap between the $s^2d$ and $sd^2$ states, which exists in free atoms of Ce, Pr, U, and Np, may decrease in a crystal or even disappear completely.

On the basis of the definition of a mixed valence state adopted in Sec. 2 the configurations $(sd)^{3-x}\tilde{f}^x_{j1}f^n_{j2}$ and $(sd)^3\tilde{f}^x_{j1}f^{n-x}_{j2}$ are not equivalent. In the former case after an allowance for the itinerant nature of the $\tilde{f}_{j1}$ states we find that the valence of an $f$ ion should be regarded as an integer equal to 3 (if we ignore a small contribution of the $\tilde{f}$ states in the inner well). In the latter case we have a true mixed valence of $3 + x$ (or $2 + x$ for the compounds formed by Sm and Eu) in spite of the formal presence of $n$ electrons of the $f$ symmetry in the pseudoatom. Interpretation of experiments of different types requires knowledge of the precise properties of the $f$ electrons. Consequently, different experiments can give different values for the mixed valence even for the same compound. The experimental methods sensitive to local characteristics of the core of an ion (for example, determination of the lattice constant) give in the former case a value close to $n$ for the number of the $f$ electrons, whereas in the latter case they give an intermediate value approximately equal to $n - x$. The methods sensitive only to the symmetry of the wave functions can give the same integer in both cases. For example, a change in the valence of Ce as a result of the $\gamma \rightarrow \alpha$ transition cannot be detected in experiments of this kind if the transition is of the $f^1_{5/2} \rightarrow f^{1-x}_{5/2}\tilde{f}^x_{7/2}$ type. It is possible that the data on the Compton scattering of $\gamma$ rays[24] should be interpreted bearing these points in mind. Photoelectron spectroscopy with angular resolution, distinguishing the band $f$ electrons from the atomic ones, can shed light in such cases.[25,26]

The energy spectrum of a Wigner–Seitz pseudoatom in a potential relief of the type shown in Fig. 7, which is characterized by lower (compared with a free atom) centrifugal barriers for the $d$ and $f$ electrons, differs considerably from the spectrum of a free atom to which the pseudoatom is genetically related. A discrete level $\varepsilon^{\mathrm{CS}}_{f_j}$ of a pseudoatom remains in the range of negative energies relative to zero of the crystal potential and the levels of the $d$ and $\tilde{f}_{\mathrm{DS}}$ electrons are above zero of this potential, but mainly lower than the "parapet" of the centrifugal potentials for $l = 2, 3$ and they form states in an atomic quasicontinuum[20] which is in resonance with the continuum of the band states from region $B$ of a crystal. We shall show that when electrons tunnel from the region $B$ to the core region $A$ of pseudoatoms with this energy spectrum, dynamic electron–polaron effects predominate in the region $A$ and these effects may modify greatly the energy spectrum of the system and be responsible for unusual phenomena, such as the presence of heavy fermions.

The Hamiltonian of a pseudoatom $A$ is

$$H_A = \sum_{m=j}^{-j} \varepsilon_{f_j}\psi^+_{f_{jm}}\psi_{f_{jm}} + U\sum_{mm'} n_{f_{jm}}n_{f_{jm'}} + \int \tilde{\varepsilon}_f\psi^+_{\tilde{f}\varepsilon}\psi_{\tilde{f}\varepsilon}S_f(\varepsilon)\,d\varepsilon + \int \varepsilon_d\psi^+_{d\varepsilon}\psi_{d\varepsilon}S_d(\varepsilon)\,d\varepsilon + H_{ff} + H_{fd} + H_{dd}, \tag{17}$$

where the last three terms describe all possible Coulomb and exchange interactions between the pseudoatom electrons, with the exception of the explicitly separated Hubbard interaction of the collapsed $f^{\mathrm{CS}}_j$ electrons; $S_f(\varepsilon)$ and $S_d(\varepsilon)$ are the partial densities of states in the atomic continuum with $l = 2, 3$. The tunneling from the region $A$ to the region $B$ is described by the Hamiltonian

$$H_{AB} = \int d\varepsilon\,\{V_{Rf}(\varepsilon)\,\psi^+_{\tilde{f}\varepsilon}\psi_{b\varepsilon} + \mathrm{H.C.}\} + \int d\varepsilon\,\{V_{Rd}(\varepsilon)\,\psi^+_{d\varepsilon}\psi_{b\varepsilon} + \mathrm{H.C.}\}, \tag{18}$$

where $\psi_{b\varepsilon}$ are the second-quantization operators for the band electrons. The Coulomb and exchange interactions of the atomic $f$ electrons with the states of the continuum, which play a decisive role in the usual theory of the Anderson and Kondo lattices,[27,28] will be ignored in order not to confuse the picture of the dynamic modification of the atomic states which are of interest to us.

The interaction between the band continuum and the atomic excitations is described by the equations

$$G=G_0(1+KG_0), \tag{19a}$$

$$KG_0=\Sigma G, \tag{19b}$$

where $G$ is the Green's function of the electrons in the band continuum, $G_0$ is the same function without allowance for tunneling, $\Sigma$ is the self-energy part of the function, and $K$ is the matrix of the reaction describing the scattering of these electrons by the states of an $f$ atom, the resolvent of which is of the form $G_A = (E-H_A)^{-1}$. In the problem of an impurity $f$ atom we have to replace the $K$ matrix, describing standing waves in a periodic crystal, with a $T$ matrix that has analytic properties corresponding to the states of scattered waves.

We shall assume that the characteristic times of such a system satisfy $\tau_{\text{tun}} < \tau_{\text{at}} < \tau_{\text{life}}$, where $\tau_{\text{tun}} \sim \hbar B_b^{-1}$ is the time for a particle to tunnel through a potential barrier of height $B_b$ separating the region $A$ from the region $B$; $\tau_{\text{at}} \sim \hbar(E_{\tilde{f}}, E_{fd})^{-1}$ is the characteristic time of the intraatomic relaxation processes ($E_{f\tilde{f}}$ and $E_{fd}$ are the excitation energies of soft atomic modes investigated in the preceding section; $\tau_{\text{life}} \sim \hbar(\Gamma_f, \Gamma_d)^{-1}$ are the characteristic lifetimes of electrons in the atomic quasicontinuum, until they escape to the outer region $B$; and the corresponding widths of the levels are given by the self-consistent solution of the many-electron problem. It is clear from the calculations of Sec. 4 that $B_b \sim \text{Ry}$, whereas $E_{f\tilde{f}} \sim E_{fd} \sim 1\text{–}3$ eV, so that the left of the inequality describing the hierarchy of times is clearly satisfied. We have to determine the conditions for the right half.

When the characteristic times obey this inequality, we can assume (see Refs. 3 and 27) that an electron tunnels to the region $A$ instantaneously. This is followed by modification of the atomic state due to the appearance of the additional particle; the modification involves processes with characteristic energies $E_{f\tilde{f}}$, $E_{fd} < B_b$, bounded below by the lifetime of that particle $\tau_{\text{life}}$ in an atom. Then, in Eq. (19b) for the $K$ matrix we need include only terms of second order in $H_{AB}$ and the problem of the scattering of an electron by an $f$ atom reduces to a calculation of the matrix elements

$$K_R(E)=\langle E, f^n | H_{AB} \frac{1}{E-H_A} H_{AB} | E, f^n \rangle, \tag{20}$$

where the bra and the ket represent states with electron excitations having the energy $E$ above the level $E_F$ of the Fermi sea and with the $f$ shell of a rare-earth atom in the configuration $f_i^n$ for the collapsed electrons. The scattering occurs independently at each site $R$.

This problem is formally similar to that of many-particle modification of atomic spectra as a result of instantaneous jolting of free $f$ atoms due to photoemission from x-ray shells[9] or of $f$ atoms in a crystal when photoemission occurs from the valence shells.[28] In the operators of the bare (unrenormalized) Hamiltonian $H_A$ the quantity $K_R(E)$ can be rewritten in the form

$$K_R(E)=(E, f^n | H_{AB} | \Lambda) \left( \Lambda \left| \frac{1}{E-H_A} \right| \Lambda \right) (\Lambda | H_{AB} | E, f^n), \tag{21}$$

where $\Lambda$ represents the complete set of eigenstates of this Hamiltonian with an integral number of electrons occupying the subshell $f_j^n$. In spite of the fact that $H_{AB}$ is formally a one-electron operator, which alters the state of just one particle, in the case of instantaneous nonadiabatic tunneling the remaining atomic states may be mixed (the pseudoatom may be jolted). This may be accompanied by processes analogous to shakedown in photoelectron spectra,[9] when the states of an atomic continuum with an excess electron, which exists in the form of soft virtual excitations in free atoms (Sec. 4), are pulled into the range of energies above the Fermi level. As in the case of discrete levels, discussed in Sec. 3, hybridization of the atomic states is governed by the Coulomb and exchange interactions in $H_A$ of Eq. (17) and then the states with an excess collapsed-state electron $f_j^{n+1}$ are largely quenched by the Hubbard repulsion and become mixed with $|f^n\tilde{f}\varepsilon)$ and $|f^n d\varepsilon)$ states from the quasicontinuum [see Eqs. (5) and (7)].

In connection with heavy fermions it is of considerable interest to consider the processes of many-particle dynamic relaxation of pseudoatoms, which are similar to giant Koster–Kronig fluctuations in the photoelectron spectra of free atoms[9] or to the Kondo resonances in the case of photoemission from Anderson lattices.[28] We shall demonstrate the appearance of such resonances by considering a situation with a valence which represents nearly an integer when $\tilde{f}_{\text{DS}}$ states remain above the Fermi level or are not realized at all, so that the states in the $d$ continuum remain and we can adopt the mean field approximation taking, for example, from the Coulomb interaction the term

$$\begin{aligned} H_{fd}^{MF} &= \int Q_{df} \langle \overset{+}{\psi}_{jm} \psi_{d\varepsilon} \rangle \overset{+}{\psi}_{d\varepsilon'} \psi_{jm} \, d\varepsilon \, d\varepsilon' + \text{H.C.} \\ &\approx \int \Delta(\varepsilon') \overset{+}{\psi}_{d\varepsilon'} \psi_{jm} + \text{H.C.} \end{aligned} \tag{22}$$

to describe the dipole relaxation of the $d$ continuum. Here, $Q_{df}$ is the Coulomb interaction integral defined by Eq. (3).

The problem of calculating the $K$ matrix of Eq. (21) reduces to finding the matrix elements of the operator $E-H_A$ and inversion of the corresponding matrix. To lowest order in $\Delta$ this operator becomes diagonalized by a linear combination of the states

$$|\Phi_R E) = f_R^{n+1}) + \int_{\hbar\tau_{life}^{-1}}^{B_b} \frac{\Delta(\varepsilon)}{E-\varepsilon} | f_R{}^n d\varepsilon) \, d\varepsilon \tag{23}$$

(see Ref. 29), which generalizes the simple expression of Eq. (5) to the case of a continuum of delocalized states allowing for the physical cutoff associated with the hierarchy of times adopted above. Then, the poles of the $K$ matrix in the $fd$ channel are described by the equation

$$E_\Lambda = \varepsilon_{f_j} + U + \int_{\Gamma_d}^{B_b} \frac{|\Delta(\varepsilon)|^2 \, d\varepsilon}{E_\Lambda - \varepsilon}, \tag{24}$$

which together with the renormalized vacant level $\varepsilon_{fj} + U$ of an excess collapsed electron gives rise to a Kondo resonance in exponential proximity to the Fermi level on condition that $\epsilon_{fj} + U > \Gamma_d$. The width of the resonance

$$\Gamma_d \approx B_b \exp\left[-(\varepsilon_f + U - E_F) B_b / \pi \Delta^2\right] \tag{25}$$

ensures in a self-consistent manner a long lifetime $\tau_{\text{life}}$ for the additional electron in the inner part of the atomic potential. Solutions of this type can appear also in the hole channel when a situation with a mixed valence is realized (left half of Fig. 7); the monopole $f\tilde{f}$ relaxation can be considered in a similar manner.

This elementary analysis was made in order to demonstrate the possible role of soft intraatomic excitons in the renormalization of the density of states on the Fermi surface. The resultant resonance in the charge channel is closer to anomalies in the x-ray absorption spectra[30] than to the usual Kondo effect, but the phenomenological manifestations are similar. Naturally, this analysis has to be generalized: we have to allow for higher orders in $\Delta$, for the dynamic fluctuations outside the mean field of the framework, for the scattering in the spin channel which is in fact an analog of the Kondo effect, etc. However, we would hope that even a more refined theory would retain the main features of the model: the presence of soft excited states in the partly filled $4f$ and $5f$ shells facilitates the appearance of one- and many-particle resonances near the Fermi level, which in the adiabatic tunneling case give rise to a mixed valence state, whereas when jolted rapidly they also give rise to heavy fermions.

## 6. CONCLUSIONS

Our numerical calculations demonstrate that the atoms of Ce, Pr, Sm, Eu, Yb, U, and Np which have compounds exhibiting a mixed valence and heavy fermions, are characterized by very labile $f$ shells and have low-lying excited states with dense electrons distributed significantly between the shells and, in particular, with a transition of one of the $f$ electrons from a normal collapsed state to a partly decollapsed state. In the case of Ce, Sm, Eu, and U these transitions occur relatively easily, whereas in the case of Pr and Np the corresponding excitations are somewhat harder to achieve. This result is correlated with the circumstance that the compounds of Pr and Np exhibiting a mixed valence and heavy fermions are found much less frequently than cerium and uranium compounds having the same properties, and also with the fact that a transition to a mixed valence state in, for example, Pr compounds would require much higher pressures than in the case of Ce compounds. It is interesting to note also that in the case of Yb there is no decollapsed $\tilde{f}$ state, so that the particle–hole symmetry in the Ce–Yb pair is not observed in the form discussed here. Clearly, a mixed valence state of Yb compounds is entirely due to the $fd$ mixing. It is possible that this accounts for the experimentally observed asymmetry of the properties of Ce and Yb compounds: states with heavy fermions in Yb compounds are found less frequently and these fermions are less heavy than in Ce compounds.

Our analysis shows also that in the solid state a dynamic polarization of shells in the course of propagation of Fermi excitations in a crystal plays a significant role, alongside direct hybridization of the states of atomic shells with the band continuum. The electron–polaron effects which then appear may exhibit a variety of forms and their explanation requires a more detailed theoretical analysis.

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