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Interaction-driven equilibrium and statistical laws in small systems: The cerium atom

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It is shown that statistical mechanics is applicable to isolated quantum systems with finite numbers of particles, such as complex atoms, atomic clusters, or quantum dots in solids, where the residual two-body interaction is sufficiently strong. This interaction mixes the unperturbed shell-model (Hartree-Fock) basis states and produces chaotic many-body eigenstates. As a result, an interaction-induced statistical equilibrium emerges in the system. This equilibrium is due to the off-diagonal matrix elements of the Hamiltonian. We show that it can be described by means of temperature introduced through the canonical-type distribution. However, the interaction between the particles can lead to prominent deviations of the equilibrium distribution of the occupation numbers from the Fermi-Dirac shape. Besides that, the off-diagonal part of the Hamiltonian gives rise to an increase of the effective temperature of the system (statistical effect of the interaction). For example, this takes place in the cerium atom, which has four valence electrons and which is used in our work to compare the theory with realistic numerical calculations. [S1063-651X(98)07804-0]

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I. INTRODUCTION

Consider a many-body quantum system of interacting particles. If the number of particles is large, statistical laws can be applied to describe the properties of the system. They can also be applied to few-particle systems (or even single particles) interacting with a heat bath. In both cases the equilibrium is achieved at arbitrarily weak interaction between the particles, or with the heat bath. If the interaction between the particles is strong enough, a different kind of statistical equilibrium is possible in isolated few-particle quantum systems. It is achieved when the excited states of the system become chaotic *compound* states. The systems examined so far are the rare-earth atom of Ce [1] with just four active valence electrons, 12 nucleons in the s-d shell [2], and $n=4-7$ particles interacting by means of a two-body random interaction [3,4]. In spite of the obvious differences these systems have much in common, as far as properties of their eigenstates and various statistics are concerned. It has been shown in [2–4] that in the regime of compound excited states one can introduce such thermodynamic parameters as temperature and entropy, and observe other typically statistical features, e.g., the Fermi-Dirac distribution of the occupation numbers.

In the present work we concentrate on the statistics of the occupation numbers in a realistic Fermi system: the atom of Ce. We show that when the interaction between the particles is strong and the two-body matrix element fluctuates strongly as a function of the single-particle states involved (hence, there is no good mean-field approximation), large deviations from the Fermi-Dirac behavior are observed. However, a statistical description of the system including the introduction of a temperature is still possible if the interaction between the particles is properly accounted for.

The notion of compound states is important for our work, so we would like to explain it in greater detail. Suppose that for a given range of excitation energies the interaction between the particles gives rise to a certain mean field. This mean field can then be used to generate a set of single-particle orbitals. The multiparticle basis states of the system can be constructed from these orbitals by simply specifying their occupation numbers. The spectrum of such states in a system with several active particles is very dense since there are many ways of distributing them among the orbitals. For the interacting particles these multiparticle states are not the eigenstates of the system. Instead, they are mixed together by the residual two-body interaction. If this interaction is strong, the number of basis states ''involved'' in almost every eigenstate of the system becomes very large (about 100 in atoms and up to 10^6 in nuclei), and the eigenstates become almost random (chaotic) superpositions of the basis states, devoid of any good quantum numbers, save the exact ones—energy, parity, total angular momentum, etc. Following the nuclear physics terminology we call such eigenstates *compound states*. Their statistical properties, e.g., distribution over the unperturbed basis states, are very similar in different systems studied: atoms, nuclei, or a two-body random interaction model. Most importantly, they provide a good starting point for developing a statistical theory for isolated few-particle systems [4].

II. STATISTICS OF THE OCCUPATION NUMBERS

Statistical behavior is usually established in the limit of a large number of particles n. Moreover, simple quantitative results can be obtained if correlations between the particles are somehow weak. This means that the interaction between the particles can be neglected, or—more realistically—an appropriate mean-field theory is developed. The latter results in the picture of free quasiparticles moving in the effective self-consistent field created by the constituents.

In the limit of large n the temperature T is a well-defined physical quantity and all equilibrium characteristics can be found by applying the canonical (Gibbs) probability distribution $w_i \propto \exp(-E^{(i)}/T)$, where $E^{(i)}$ is the energy of the ith eigenstate of the system. For example, for a gas of noninteracting fermions this results in the famous Fermi-Dirac distribution (FDD) of the occupation numbers:

$$\overline{n}_\alpha=\frac{1}{\exp[(\varepsilon_\alpha-\mu)/T]+1}, \tag{1}$$

where ε_α is the energy of a single-particle state α, and $\mu=\mu(n,T)$ is the chemical potential. It is determined, at a given temperature, from the normalization condition $\Sigma_\alpha\overline{n}_\alpha=n$. Formula (1), when it is valid, in fact provides one with a relation between the temperature and the energy E of the system: $\Sigma_\alpha\varepsilon_\alpha\overline{n}_\alpha=E$, which can also be viewed as a possible definition of the temperature. Note that Eq. (1) can hold for the interacting fermions as well, provided we consider the distribution of *quasiparticles*, and replace ε_α with the quasiparticle energy $\tilde{\varepsilon}_\alpha$, which in turn depends on the distribution of excited quasiparticles. This is an important point of Landau's theory of Fermi liquids (see, e.g., [5]).

Strictly speaking, the FDD is derived for the grand canonical ensemble, where μ is fixed, and n is the mean number of particles [6]. For large n the difference is negligible unless fluctuations of the number of particles are concerned. In the Appendix we consider the approximations one has to make to arrive at the FDD (1) for a finite system of n interacting particles obeying the canonical distribution.

In reality there are many complex systems, such as compound nuclei, rare-earth atoms, molecules, atomic clusters, or quantum dots, which do not satisfy the conditions for Eq. (1) to hold. However, their complexity suggests that some statistical methods can be developed, and in nuclear physics such a statistical temperature-based description has been known for quite a while. Intuitively such a description is very natural, and a more rigorous justification does not seem to have been needed.

The number of active particles in these systems can be relatively small ($\lesssim 10$), whereas the interaction between them (even the residual interaction in the mean-field basis) is large, i.e., greater than the energy intervals between unperturbed many-particle basis states. This interaction makes up for the absence of a heat bath, and promotes the onset of ''randomization'' and quantum chaos. This chaos is purely dynamical, in the sense that the Hamiltonian matrix of the system does not contain any random parameters, yet the behavior can be complicated enough (''chaotic''), and a number of properties, e.g., the energy level statistics, are consistent with the predictions of random matrix theories [1–3]. This gives one a possibility to talk about some kind of equilibrium in the system, and pursue the development of a statistical theory for few-body Fermi systems [4].

In what follows we will look at the results obtained numerically in a realistic model of the Ce atom which contains only four active particles (valence electrons). We will see that the energy dependence of the occupation numbers differs prominently from what one expects from the FDD (1), and show that this behavior results from the strong fluctuations of the two-body Coulomb interaction for different orbitals. We then show that this interaction can be taken into account within the statistical approach to calculation of the occupation numbers and other mean values, leading to a good agreement between the results of our *statistical* theory and the numerical calculations. Such agreement confirms the existence of equilibrium similar to the thermal one in the system of a few strongly interacting particles.

III. THE Ce ATOM

The cerium atom has one of the most complicated spectra in the periodic table. The density of energy levels with a given total angular momentum and parity J^π reaches hundreds of levels per eV at excitation energies of just a few eV, well below the ionization threshold of $I=5.539$ eV [7,8]. The Ce atom has four valence electrons, and a well-defined $4f6s^25d$ ground state. However, with the increase of the excitation energy and involvement of yet another low-lying electron orbital $6p$, the atomic eigenstates become compound states (in the sense of Sec. I), and it becomes absolutely impossible to choose any reasonable coupling scheme or provide any classification for them. At the same time, the orbital occupation numbers move away from integer values, and even the idea of a dominant configuration for a particular energy level becomes meaningless [1].

In the present work we continue to study the cerium atom numerically, with emphasis on the energy dependence of the occupation numbers. The electronic structure of the Ce atom consists of a Xe-like $1s^2\cdots5p^6$ core and four valence electrons. A large difference in the energy scales of the core and valence electrons allows us to neglect excitations from the core and consider the wave function of the core as a ''vacuum'' state $|0\rangle$. Accordingly, the four active electrons added to this vacuum form the spectrum of Ce at excitation energies $E\lesssim I$ [9].

The calculations are performed using the Hartree-Fock-Dirac (HFD) and configuration interaction (CI) methods (see [1] for details). A self-consistent HFD calculation of the neutral atom results in the construction of the core and valence orbitals. It also determines the mean-field potential, which is then used to calculate the basis set of single-particle orthonormalized relativistic states $|\alpha\rangle=|nljj_z\rangle$ with energies ε_α. This procedure defines the zeroth-order Hamiltonian of the system,

$$\hat{H}^{(0)}=\sum_\alpha \varepsilon_\alpha a_\alpha^\dagger a_\alpha. \tag{2}$$

The unperturbed multiparticle basis states $|k\rangle$ constructed from the single-particle states, $|k\rangle=a_{\nu_1}^\dagger a_{\nu_2}^\dagger a_{\nu_3}^\dagger a_{\nu_4}^\dagger|0\rangle$, are eigenstates of $\hat{H}^{(0)}$: $\hat{H}^{(0)}|k\rangle=E_k^{(0)}|k\rangle$, where

$$E_k^{(0)}=\sum_\alpha \varepsilon_\alpha n_\alpha^{(k)} \tag{3}$$

is the zeroth-order energy of the state $|k\rangle$, and $n_\alpha^{(k)}=\langle k|\hat{n}_\alpha|k\rangle=\langle k|a_\alpha^\dagger a_\alpha|k\rangle$ are the occupation numbers equal to 0 or 1, depending on whether the state α is occupied in $|k\rangle$, or not. To subtract additional symmetries only the basis states $|k\rangle$ with a given projection of the total angular momentum J_z and parity are considered.

The total Hamiltonian $\hat{H}$ of the active electrons is the sum of the zeroth-order mean-field Hamiltonian $\hat{H}^{(0)}$ and the two-body residual interaction

$$\hat{V}=\frac{1}{2}\sum_{\alpha\beta\gamma\delta} V_{\alpha\beta\gamma\delta}a_\alpha^\dagger a_\beta^\dagger a_\gamma a_\delta. \tag{4}$$

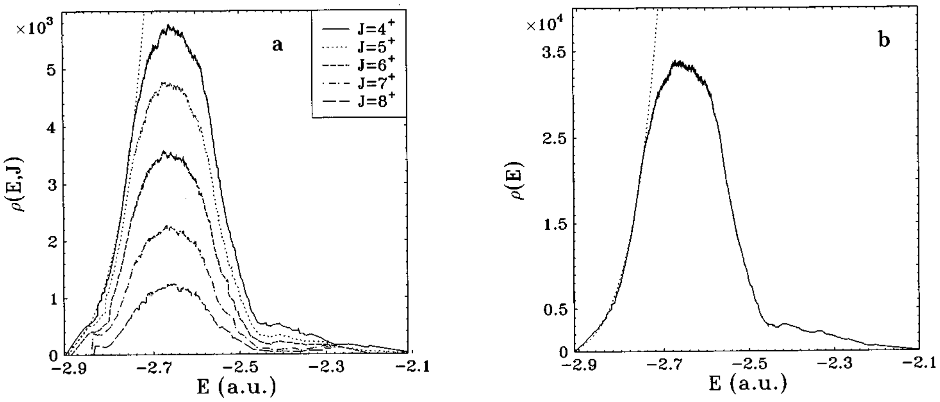

FIG. 1. Eigenvalue densities for the even states of Ce averaged over the energy interval $\Delta E = 0.05$ a.u. (a) The upper solid curve is for $J=4$, and lower curves correspond to successively increasing values of J. Note that all densities have similar shapes. Dotted curve is the analytical fit for $J=4$: $\rho(E) = \rho_0 \exp[a(E-E_g)^{1/2}]$, where $\rho_0 = 27$, $a = 12.3$ a.u., and $E_g = -2.91$ a.u. (b) Total level density of the even states and fit with $\rho_0 = 119$, $a = 13.0$ a.u., and $E_g = -2.91$ a.u.

The residual interaction $\hat{V}$ contributes to the diagonal and off-diagonal matrix elements between the multiparticle states $|k\rangle$. Its diagonal part shifts the energy of the basis state k,

$$\Delta E_k = V_{kk} = \sum_{\alpha > \beta} (V_{\alpha\beta\beta\alpha} - V_{\alpha\beta\alpha\beta}) n_\alpha^{(k)} n_\beta^{(k)} . \tag{5}$$

The off-diagonal matrix elements $V_{k'k} = \langle k'|\hat{V}|k\rangle$ are responsible for mixing of the multiparticle basis states.

Complete diagonalization of the operator $\hat{H} = \hat{H}_d + \hat{V}$ in the space of the basis states $|k\rangle$ yields "exact" energies $E^{(i)}$ and stationary states $|i\rangle$ [20],

$$\hat{H}|i\rangle = E^{(i)}|i\rangle, \tag{6}$$

which can be presented as superpositions of the unperturbed basis states,

$$|i\rangle = \sum_k C_k^{(i)}|k\rangle, \quad \sum_k |C_k^{(i)}|^2 = 1. \tag{7}$$

In this work we included 14 relativistic subshells nlj in the single-particle basis ($6s$, $7s$, $6p$, $7p$, $5d$, $6d$, $4f$, and $5f$), and performed exact diagonalization of the $N \times N$ Hamiltonian matrix in a Hilbert space with $N \sim 8 \times 10^3$, obtained by truncating the complete set of the shell-model atomic configurations. Our numerical results are obtained for the even states of Ce with the total angular momentum projection set to $J_z = 0$. Thereby, all possible states with J from 0 to 10 are included. For the given choice of the basis the numbers of eigenstates with $J = 0$–10 are 343, 917, 1354, 1493, 1433, 1153, 826, 497, 262, 107, and 34, respectively.

The eigenvalue densities $\rho_J(E)$ for $J = 4$–8 are shown in Fig. 1. They have been window averaged over $\Delta E = 0.05$ a.u. to smooth out short-range fluctuations. The largest density is observed for $J=4$, and with the exception of small regions near the ends of the spectra, all $\rho_J(E)$ are proportional to each other. The shapes of the eigenvalue densities are basically determined by the corresponding basis-state densities (although the effect of level repulsion makes the former slightly wider). They are characterized by a very rapid increase in the low-energy part. This increase is a direct consequence of the fact that the accessible energy can be distributed in an ever greater number of ways between the four electrons. Being essentially of combinatorial nature, the level density can be described by the exponent

$$\rho(E) \propto \exp(a\sqrt{E - E_g}), \tag{8}$$

which is derived in the independent-particle model [10] (E_g is the ground-state energy). As seen from Fig. 1 the level density from our calculation indeed follows Eq. (8) at low energies, but then reaches its maximum and decreases [11]. These latter features are unphysical as they are consequences of the finite size of our basis. However, within 5 eV of the ground state the configuration set we use is reasonably complete.

Relativistic atomic subshells nlj are $(2j+1)$ degenerate, therefore we consider average occupation numbers

$$\hat{n}_s = g_s^{-1} \sum_{\alpha \in s} \hat{n}_\alpha = g_s^{-1} \sum_{\alpha \in s} a_\alpha^\dagger a_\alpha , \tag{9}$$

where $g_s = 2j+1$ is the degeneracy of the subshell s. In the system of a large number of weakly interacting particles thermally averaged values of n_s are given by the FDD (1). In the quantum dynamical system, like the Ce atom, the occupation numbers for any eigenstate can be obtained as $n_s^{(i)} = \langle i|\hat{n}_s|i\rangle$. When the number of active particles is small $n_s^{(i)}$ show strong level-to-level fluctuations, and it is more instructive to look at the spectrally averaged values

$$n_s(E) = \overline{\langle i|\hat{n}_s|i\rangle} = \sum_k \overline{|C_k^{(i)}|^2} \langle k|\hat{n}_s|k\rangle, \tag{10}$$

where the overbar means averaging over the eigenstates i within some energy interval around E.

A typical distribution of the occupation numbers calculated at the excitation energy of 4.5 eV above the atomic ground state is shown in Fig. 2 as a function of the single-particle energy ε_s of the orbitals (see Table I). The values of ε_s are determined with respect to the Xe-like Ce^{4+} core. One can see that the distribution does not look at all like a monotonically decreasing FDD. A similar picture is observed over the whole energy interval from the ground state to the ionization potential. For example, the lowest even state of Ce has a configuration of $4f^2 6s^2$, while the FDD would tell us that all four electrons must be placed in the lowest $4f$ orbital, when the energy or "temperature" of the system is low. In reality the $4f^4$ electron configuration lies at very high energies due to a strong electron repulsion in this compact orbital (the radius of the $4f$ orbital in Ce is at least two times smaller than that of any other valence orbital).

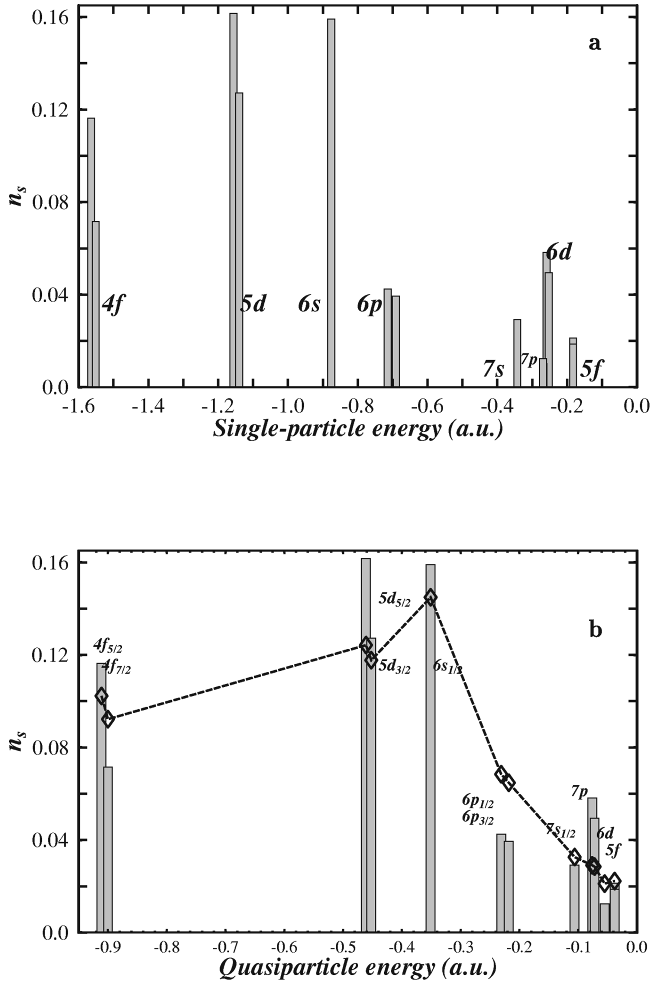

FIG. 2. Occupation numbers $n_s(E)$ [see Eq. (10)], for the even states of Ce at the excitation energy of $E-E_g=4.5$ eV versus the single-particle energies ε_s of the orbitals (a), and quasiparticle energies $\tilde{\varepsilon}_s$ (b). Diamonds connected by the dashed line represent the result of our statistical calculation with $T=0.097$ a.u.

Of course, considering the orbital energies ε_s has the drawback that they completely ignore the residual interaction between the valence electrons. When this interaction is strong one would wish to introduce some new mean-field orbital energies $\tilde{\varepsilon}_s$ that would incorporate the effect of such interaction. The value of $\tilde{\varepsilon}_s$ for the orbital s will inevitably depend on the distribution of the other electrons, and hence on the excitation energy of the system. In Sec. V we introduce such energies within the statistical approach. However, even when the occupation numbers are plotted against $\tilde{\varepsilon}_s$ there is still a large deviation from the standard FDD.

At first sight such a strong deviation from the FDD in a strongly interacting Fermi system speaks against any possibility of a statistical description of the system. In what follows we show that the strong Coulomb interaction between the electrons can be incorporated in the canonical-ensemble description of the system, and thermally averaged occupation numbers can be $n_s(T)$ derived. As a result of the electron interaction, the distribution of $n_s(T)$ differs from the FDD. What is more important, we find good agreement between the results obtained by means of this statistical approach and those from the pure dynamic calculation of the Ce eigenstates, $n_s(T)\approx n_s(E)$. We also find a way to relate the energy and the temperature.

TABLE I. Single-particle energies and Coulomb matrix elements (in atomic units) for the valence and lowest excited orbitals in Ce.

Orbital *nlj*	ε_s (a.u.)	Coulomb matrix elements U_{sp}(a.u.) $4f_{5/2}$	$4f_{7/2}$	$6s_{1/2}$	$4d_{3/2}$	$4d_{5/2}$	$6p_{1/2}$	$6p_{3/2}$
$4f_{5/2}$	-1.564	0.791	0.800	0.260	0.423	0.422	0.223	0.216
$4f_{7/2}$	-1.551	0.800	0.787	0.259	0.428	0.416	0.223	0.215
$6s_{1/2}$	-0.876	0.260	0.259	0.199	0.231	0.230	0.162	0.158
$4d_{3/2}$	-1.156	0.423	0.428	0.231	0.330	0.331	0.200	0.198
$4d_{5/2}$	-1.141	0.422	0.416	0.230	0.331	0.325	0.204	0.195
$6p_{1/2}$	-0.714	0.223	0.223	0.162	0.200	0.204	0.169	0.157
$6p_{3/2}$	-0.691	0.216	0.215	0.158	0.198	0.195	0.157	0.156

IV. CANONICAL ENSEMBLE AND THE STRENGTH FUNCTION

In this section we show that averaging over the *canonical distribution*, which weighs different states according to their energies E_k with probabilities $w_k\propto\exp(-E_k/T)$, is very similar to averaging over the exact eigenstates $|i\rangle$, when these eigenstates are *compound*, i.e., include large numbers N_c of basis states $|k\rangle$ mixed together with small weights $C_k^{(i)}\sim 1/\sqrt{N_c}$, Eq. (7). For a classical system the latter is equivalent to averaging over the *microcanonical distribution* that considers all points on the surface $E=\text{const}$ of the phase space as equally probable [12]. As is known, the two types of averaging yield identical results for large systems [6].

A. Averaging over the canonical distribution at a given temperature

Suppose first that the off-diagonal part of the residual two-body interaction $\hat{V}$ is switched off. The multiparticle basis states $|k\rangle$ then correspond to the stationary states of the system with energies $E_k=E_k^{(0)}+\Delta E_k$. The interaction with a heat bath at temperature T results in the canonical distribution of probabilities of finding the system in a given state k, $w_k=Z^{-1}\exp(-E_k/T)$, where $Z=\Sigma_k\exp(-E_k/T)$, so that $\Sigma_k w_k=1$. The occupation numbers at temperature T are calculated as

$$n_s(T)=\sum_k w_k\langle k|\hat{n}_s|k\rangle=Z^{-1}\sum_k \exp(-E_k/T)\langle k|\hat{n}_s|k\rangle. \tag{11}$$

The spectrum of E_k is similar to the eigenvalue spectra shown in Fig. 1, and is characterized by a rapid rise of its density [see Eq. (8)]. Thus, if we replace summation in Eq. (11) by integration over E_k,

$$n_s(T)=\int w_T(E_k)\langle k|\hat{n}_s|k\rangle dE_k, \tag{12}$$

where we introduced the probability density $w_T(E_k)=Z^{-1}\exp(-E_k/T)\rho(E_k)$, the integrand in Eq. (12) will peak strongly due to competition between the two exponents, the decreasing $\exp(-E_k/T)$ and the rising $\rho(E_k)$. As a result, the main contribution to $n_s(T)$ is given by the vicinity of the maximum of $w_T(E_k)$. The equation for the position of the maximum $E_k = E$ provides a relation between the most probable energy E and the temperature,

$$-\frac{1}{T}+\frac{d\{\ln[\rho(E)]\}}{dE}=0. \tag{13}$$

If the temperature is not too small the maximum of $w_T(E_k)$ is almost symmetric, and the most probable energy becomes close to the mean energy:

$$E \approx \overline{E}(T)=\int E_k w_T(E_k)dE_k . \tag{14}$$

If we use the analytical form (8), Eq. (13) yields

$$T=\frac{2}{a}\sqrt{E-E_g}. \tag{15}$$

B. Strength function and averaging over the compound states

Let us now come back to the dynamic description of the isolated many-body quantum system and switch on the off-diagonal part of the residual interaction. In this case the eigenstates are given by Eq. (6) and the occupation numbers at a given energy are found from Eq. (10). The key quantity in calculating $n_s(E)$ is the mean-squared eigenstate component $\overline{|C_k^{(i)}|^2}$. When $\hat{V}$ is strong enough and the energy $E^{(i)}$ is not too close to the ground state, $\overline{|C_k^{(i)}|^2}$ represents the spreading of the eigenstate over a large number of basis states. It is proportional to the strength function (introduced by Wigner [13] and also known as the local density of states),

$$\rho_w(E,k)=\sum_i |C_k^{(i)}|^2\delta(E-E^{(i)})\simeq\overline{|C_k^{(i)}|^2}\rho(E), \tag{16}$$

where $\rho(E)$ is the eigenvalue density. The last equality in Eq. (16) implies that some averaging over the the energy interval greater than the level spacing has been performed at $E^{(i)} \approx E$. It follows from numerical calculations [1,2,4] as well as from analytical considerations [10,13,14] that $\rho_w(E,k)$ is a bell-shaped function centered at $E \approx E_k$. Near its maximum it depends only on the difference $E-E_k$, and can be described by the Breit-Wigner formula

$$\rho_w(E,k)=\frac{\Gamma/2\pi}{(E-E_k)^2+\Gamma^2/4}. \tag{17}$$

The *spreading width* Γ is usually given by $\Gamma \simeq 2\pi|\langle k'|\hat{V}|k\rangle|^2\rho(E)$. Therefore the basis states are strongly mixed together by the residual interaction only locally, within the energy range Γ.

The notions of the strength function and the spreading width become meaningful if the interaction is strong enough, and $\Gamma \gg D$, where $D = 1/\rho(E)$ is the mean level spacing (accordingly, $\overline{|\langle k'|V|k\rangle|^2} \gg D^2$). This means that the number of basis states participating in a given eigenstate is large, $N_c \sim \Gamma/D \gg 1$, or vice versa, a given basis state k contributes to a large number of nearby eigenstates with energies $|E-E_k| \sim \Gamma$. Apart from the smooth variation of $\overline{|C_k^{(i)}|^2}$ the statistics of the eigenstate components $C_k^{(i)}$ is close to Gaussian [1]. In this situation it is appropriate to call the stationary states of the system *chaotic* or *compound* eigenstates.

Using Eq. (16) we can rewrite expression (10) for the occupation numbers in the integral form

$$n_s(E)=\int \overline{|C_k^{(i)}|^2}\langle k|\hat{n}_s|k\rangle\rho(E_k)dE_k \approx \int \rho_w(E,k) \times\langle k|\hat{n}_s|k\rangle dE_k , \tag{18}$$

where we used the fact that $\rho(E_k) \approx \rho(E)$ near the maximum of $\rho_w(E,k)$. The above representation is very similar to Eq. (12) for $n_s(T)$. Equation (18) describes averaging over the compound state strength function $\rho_w(E,k)$ of width Γ centered at energy E, whereas Eq. (12) refers to a thermal average with the $w_T(E_k)$ probability density, which peaks near $\overline{E}(T)$. Of course, the width of the distribution $w_T(E_k)$ depends on the temperature [$\sim aT^{3/2}$ for Eqs. (8) and (15)], but if we choose the temperature by setting $E = \overline{E}(T)$, the two averages $n_s(E)$ and $n_s(T)$ should be close to each other, provided the widths of $\rho_w(E,k)$ and $w_T(E_k)$ are much greater than the multiparticle level spacing, and the difference between these widths does not exceed the single-particle energy interval in the system [4].

In the next section we calculate thermally averaged occupation numbers and establish a relation between the effective temperature T and the excitation energy for the Ce atom. Numerical calculations will confirm that a temperature-based statistical theory agrees with the dynamic calculation, and describes well the peculiar behavior of the occupation numbers in Ce.

V. CALCULATION OF THERMALLY AVERAGED OCCUPATION NUMBERS

A. Statistical model

Let us now perform a statistical calculation of the occupation numbers for a system of n particles distributed over r orbitals with energies ε_s and degeneracies $g_s (s=1,\ldots,r)$. We will assume that the two-body interaction of any two particles in the orbitals s and p is U_{sp}, where both the direct and exchange terms are included:

$$U_{sp}=\frac{1}{g_s(g_p-\delta_{sp})}\sum_{\alpha\in s}\sum_{\beta\in p}(V_{\alpha\beta\beta\alpha}-V_{\alpha\beta\alpha\beta}). \tag{19}$$

Thus U_{sp} is averaged over the degenerate single-particle states within the orbitals s and p.

The energy of a particular many-particle state k is now given by

$$E_k=\sum_{s=1}^{r}\mathcal{N}_s\varepsilon_s+\sum_{s=1}^{r}\sum_{p=s}^{r}\frac{\mathcal{N}_s(\mathcal{N}_p-\delta_{sp})}{1+\delta_{sp}}U_{sp}, \tag{20}$$

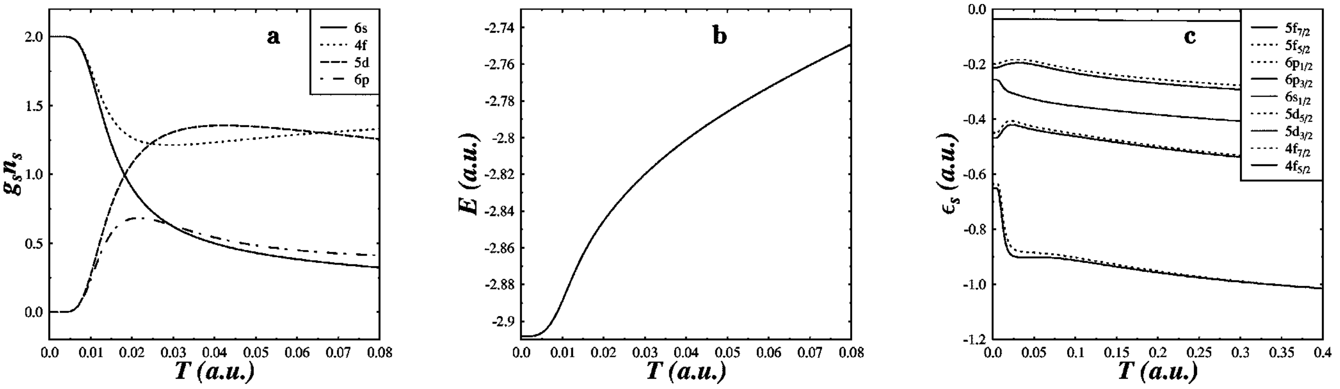

FIG. 3. Temperature dependence of the occupation numbers for the orbitals $g_s n_s(T)$ (a), energy of the system $\overline{E}(T)$ (b), and quasiparticle energies $\tilde{\varepsilon}_s$ (c), calculated in the statistical model of the Ce atom, Eqs. (20)–(24). The occupation numbers shown for the $4f$, $5d$, and $6p$ subshells are sums of those of their fine-structure sublevels $j=l\pm\frac{1}{2}$. The quasiparticle energies of the orbitals are listed in (c) in the same order as they appear on the graph.

where $\mathcal{N}_s$ is an integer number of particles in the orbital $s(0\leqslant\mathcal{N}_s\leqslant g_s)$, and $\Sigma_s\mathcal{N}_s=n$. The state k is specified by the orbital occupation numbers $\mathcal{N}_s$ and is G_k degenerate, where $G_k=\Pi_{s=1}^{r}\binom{g_s}{\mathcal{N}_s}$. Of course, Eq. (20) corresponds to the "diagonal" approximation ($E_k\approx H_{kk}$), since we neglect the effect of mixing of states due to the residual interaction (off-diagonal part of the Hamiltonian). In the low-energy part of the spectrum this interaction pushes the eigenstates down with respect to their diagonal-approximation values because of the usual level-repulsion effect.

In this model we cannot keep hold of the total angular momentum, so our calculation will yield quantities averaged over various angular momenta J and projections J_z. However, it is relatively easy to ensure the conservation of parity. If the orbital s has a parity of P_s (either 1 or -1), the parity of the multiparticle state k is $\Pi_{s=1}^{r}P_s^{\mathcal{N}_s}$. Therefore one can easily select multiparticle states with a given parity when calculating statistical sums like that of Eq. (11).

In the canonical ensemble the probability of finding the system in the state k is given by

$$w_k=Z^{-1}G_k\exp(-E_k/T), \tag{21}$$

where

$$Z=\sum_k G_k\exp(-E_k/T), \tag{22}$$

and the sum over k runs over all multiparticle states, possibly with a restriction on parity. The average occupation numbers $n_s(T)=\overline{\mathcal{N}_s}/g_s$ are calculated as

$$n_s(T)=g_s^{-1}\sum_k \mathcal{N}_s^{(k)}w_k, \tag{23}$$

where $\mathcal{N}_s^{(k)}$ is the number of particles in the orbital s in the multiparticle state k. In the diagonal approximation the energy of the system is related to the temperature as $E=\overline{E}(T)$, where

$$\overline{E}(T)=\sum_k E_k w_k \tag{24}$$

is the canonical average. However, one can include the off-diagonal part of the Hamiltonian in the definition of temperature by introducing the energy shift $\Delta_E(T)$,

$$E=\overline{E}(T)-\Delta_E(T). \tag{25}$$

$\Delta_E(T)$ is positive in the lower half of the spectrum, which means that the statistical effects of interaction between particles increase the effective temperature. At high temperatures $\Delta_E(T)=2\langle H_{ii}-E^{(i)}\rangle$, where $H_{ii}-E^{(i)}$ is the simple energy shift due to the nondiagonal matrix elements of the Hamiltonian H_{ik}. This estimate is based on the mean energy of the components $|k\rangle$ in the eigenstate $|i\rangle$: $(\overline{E_k})_i\equiv\Sigma_k H_{kk}|C_k^{(i)}|^2=E^{(i)}+\Delta_E$ (see [4]).

In general, the occupation numbers obtained from Eq. (23) will be different from those predicted by the Fermi-Dirac distribution (see Sec. V B). In the Appendix we look at how the FDD (1) is derived from the canonical statistical distribution, Eq. (23), and see what are the limitations on the interaction between the particles for the derivation to be valid.

B. Numerical calculations

To perform numerical calculations of the occupation numbers for Ce in the statistical model outlined above we use the same set of 14 relativistic orbitals as in the CI calculation described in Sec. III. The orbital energies are obtained as $\varepsilon_s=\langle s|H_c|s\rangle$, where H_c is the frozen Dirac-Fock Hamiltonian of the Ce^{4+} core, and the averaged Coulomb matrix elements U_{sp} are found from Eq. (19). Their numerical values for the seven lowest orbitals $4f_{5/2}$, $4f_{7/2}$, $6s_{1/2}$, $5d_{3/2}$, $5d_{5/2}$, $6p_{1/2}$, and $6p_{3/2}$ are given in Table I. For excitation energies below the ionization threshold these orbitals are the most important.

Using the statistical model formulas we have calculated the occupation numbers $n_s(T)$, Eq. (23), and the energy of the system, Eq. (24), as functions of T [see Figs. 3(a) and 3(b)]. The relation between the energy of the system and temperature $E=\overline{E}(T)-\Delta_E(T)$ can be inverted and used to plot the dependence of the statistical model occupation numbers as functions of the energy E. In this work we are mostly

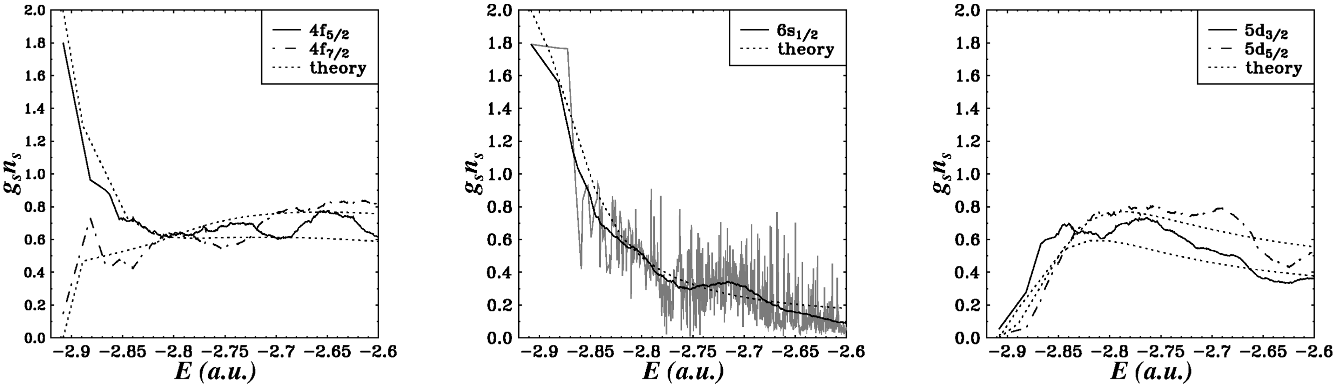

FIG. 4. Comparison of the orbital occupancies $g_s n_s(E)$ obtained from the exact diagonalization (solid and dash-dot lines) with $g_s n_s(T(\overline{E}))$ obtained from our statistical theory (dotted lines). Note that $n_s(E)$ have been window averaged over $\Delta E = 0.05$ a.u. For the $6s_{1/2}$ orbital the solid gray line connects unaveraged occupation numbers for the eigenstates with $J=4$.

interested in the low-energy part of the spectrum, and we set $\Delta_E(T) = \text{const}$ to fit the true ground-state energy of the system at $T=0$. In Fig. 4 we compare the results of the statistical model with the energy-averaged occupation numbers obtained from the CI calculation of the Ce eigenvalues and eigenstates, Eqs. (6) and (10). We see that the complicated non-Fermi-Dirac energy dependence of the occupation numbers in Ce is reproduced well by the statistical model.

For one of the orbitals unaveraged occupation numbers are shown in Fig. 4. For a chaotic eigenstate with about N_c principal components the fluctuations of various quantities are expected to be $\sim N_c^{-1/2}$. If the average occupation number $\overline{n_s}$ is smaller than unity, the s orbital is populated only in about $\overline{n_s} N_c$ of the basis states involved, and the relative fluctuation of the occupation number can be estimated as $\delta n_s \sim 1/\sqrt{\overline{n_s} N_c}$. For Ce where $N_c \sim 100$ this estimate is in agreement with the size of fluctuations seen for the $6s_{1/2}$ orbital in Fig. 4.

To study the effect of the off-diagonal matrix elements of the Hamiltonian on the temperature we calculate the canonically averaged mean energy of the system (24) using the set of the basis-state energies $E_k \equiv H_{kk}$ and that of the exact eigenstates $E^{(i)}$. The difference between these two mean energies is plotted in Fig. 5. It is almost constant at small temperatures and follows

$$\Delta_E(T) \simeq \frac{\overline{\Sigma_{k \neq l} H_{kl}^2}}{T}, \tag{26}$$

at large T (see [4]).

Note that the energy shift $\Delta_E(T)$ is larger than the simple difference between the diagonal matrix elements and exact eigenvalues $H_{ii} - E^{(i)}$. This is because the true occupation numbers (10) even in the exact ground state are not integer (see Fig. 4) due to the admixture of higher configurations. This means that the effective temperature of the ground state is already not zero (see discussion in [4]).

VI. DISCUSSION AND CONCLUSIONS

Most importantly, the agreement observed in Fig. 4 means that the interaction between the particles indeed introduces some kind of equilibrium in the system (''microcanonical'' distribution). Moreover, averaging over it yields results close to those over a canonical ensemble (21), with the temperature chosen to reproduce the total energy of the system. This equivalence is always true for a large system where any albeit weak interaction between particles leads to equilibrium. However, in a *few-particle* system the residual two-body interaction must be *strong enough* to produce chaotic eigenstates and facilitate statistical description (see [15–17] where criteria for the interaction strength are discussed).

The simple criterion for the onset of ''chaos'' follows from the perturbation theory:

$$\alpha \equiv \frac{V}{D_2(E)} = \sqrt{S} \frac{\sqrt{\overline{H_{ik}^2}}}{D(E)} \gtrsim 1, \tag{27}$$

where $D_2(E) = D(E)/S$ is the mean energy spacing between many-body basis states directly coupled by a nonzero off-

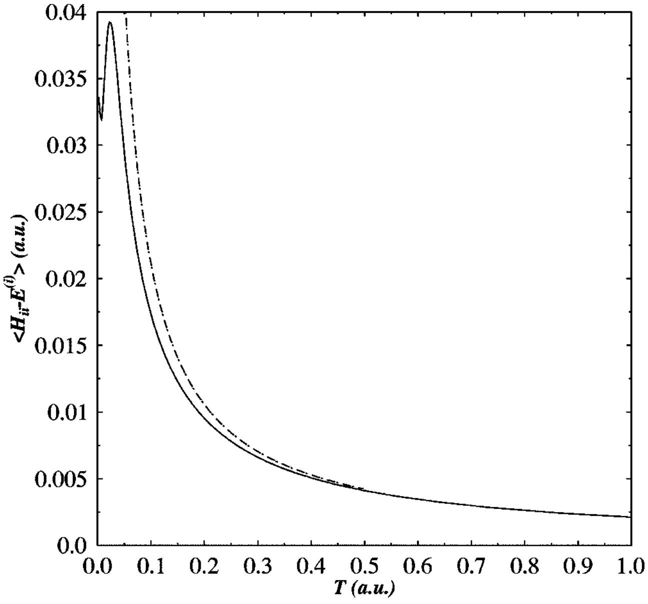

FIG. 5. Difference between the mean values of the energy obtained from the canonical distribution using the energies of the basis states, $E_k \equiv H_{kk}$, and those of the exact eigenstates. The dash-dot line is the high-temperature analytical approximation (26).

diagonal matrix element, V is the root-mean-squared nonzero off-diagonal matrix element, and $S<1$ is the sparsity of the Hamiltonian matrix defined as a fraction of nonzero off-diagonal matrix elements, $\overline{H_{ik}^2}=SV^2$. The Hamiltonian matrix is sparse because the residual Coulomb interaction between the valence electrons is a two-body one, hence for more than two excited electrons not all many-body basis states can be coupled in the lowest first order.

In our numerical model α becomes greater than unity at $E-E_g>0.07$ a.u., i.e., above 2 eV from the ground state. This energy is of the order of energy spacing between the single-electron orbitals in Ce. Note that the estimates from [15–17] can hardly be applied to our model. The point is that in our system there are additional degrees of freedom and symmetries (angular momentum, its projection and parity), while [15–17] in fact considered a system without any symmetries (an effective one-dimensional system). As a result, the single-particle levels are multiply degenerate. An additional chaotization of the many-body state basis takes place when complex linear combinations of the Slater determinants are constructed to form basis states with definite angular momentum values. As noted in [2], this procedure involves randomlike Clebsch-Gordan coefficients. On the other hand, comparison with estimates near the Fermi surface [16] is difficult due to the fact that the very concept of the Fermi energy is ill defined for such a small system with strong interaction (see Fig. 2).

We would like to reiterate now, that although the temperature-based description is applicable to our four-particle system, the orbital occupancies could not be described by the FDD (Fig. 2). The FDD is inapplicable to our system because of the strong interaction between the particles [second term on the right-hand side of Eq. (20)]. However, the deviation from the FDD is determined not by the magnitude of U_{sp}, but rather by the size of their fluctuations. To see this assume for a moment that all two-body matrix elements are the same, $U_{sp}\equiv U$. In this case the double sum in Eq. (20) just shifts all energies by $(U/2)n(n-1)$, and the statistical properties of the system are the same as for non-interacting particles. If U_{sp} are different for different orbital pairs sp one can still introduce some average interaction $\overline{U}$ and subtract this ''background'' interaction from the interaction term in Eq. (20). This procedure effectively suppresses the interaction term, since the summands in expressions like $\Sigma_{s<p}(U_{sp}-\overline{U})\mathcal{N}_p$ have different signs. Note that the introduction of (energy-dependent) $\overline{U}$ is equivalent to a local mean-field approximation (see also the Appendix). This approximation is good if the fluctuations of U_{sp} from one orbital to another are relatively small.

An instructive example was provided in [3,4]. In these works a model of random two-body interactions was explored numerically and a good Fermi-Dirac-like behavior of the occupation numbers was observed for as few as four particles distributed among 11 orbitals. However, this regime was achieved for the relatively small two-body matrix elements with mean zero and rms $V\sim 0.1d_1$, where d_1 is the mean level spacing between the single-particle orbitals. On the other hand, for smaller two-body interaction strengths the occupation number distribution was not smooth, and did not agree well with the Fermi-Dirac formula, because the statistical equilibrium needed was not achieved.

The situation in the Ce atom is different. The $4f$ orbital has a much smaller radius than any other orbital, and the Coulomb interactions have a hierarchy of scales:

$$U_{4f4f}>U_{4fs}>U_{sp}, \tag{28}$$

where s and p are orbitals other than $4f$. Indeed, the Coulomb interaction between the electrons is determined mostly by the mean radius of the largest orbital. Thus, for the two orbitals s and p such that $r_s<r_p$, the Coulomb interaction is $U_{sp}\approx e^2/r_p$ (this formula is exact for the two electrons distributed uniformly over the surfaces of two spheres of radii r_s and r_p). Because of Eq. (28) the interaction term in Eq. (20) fluctuates strongly with the change of the occupation number of the $4f$ orbital, and in effect there is no good mean-field approximation for the excitation spectrum of Ce. The quasiparticle orbital energies $\tilde{\varepsilon}_s$ can still be obtained in the statistical model for Ce by means of Eq. (A10). They are plotted in Fig. 3(c) and show considerable variation with temperature. However, even when we use these energies instead of the Hartree-Fock ones for plotting the occupation numbers, the resemblance to the true FDD is only marginally better than that in Fig. 2.

The absence of reasonably defined quasiparticle orbitals and the ensuing distortion of the Fermi-Dirac distribution are features outside the usual Migdal theory of normal finite Fermi systems (TFFS) [18]. Its breakdown in the Ce atom can be associated with the open-shell structure of the atom (nearly degenerate ''ground state'') and a clear lack of symmetry of the ground state with one removed particle. As a result, single-particle excitations above the ground state do not carry good quantum numbers (like the momentum in an infinite Fermi system, or the angular momentum in a spherically symmetric finite system). Moreover, even at low energies (few eV) the single-particle excitations have large widths associated with their decay into multiply excited configurations (the spreading width $\Gamma\sim 2$ eV [1]), largely because such decay is not really limited by any selection rules (only the trivial total angular momentum and parity are conserved).

It has been proposed in [4] that for finite Fermi systems similar to the Ce atom, characterized by the dense spectra of chaotic multiparticle eigenstates, a statistical theory alternative to the standard TFFS can be developed based on the properties of these eigenstates. Most importantly, the existence of the chaotic eigenstates and the equilibrium this introduces in the system is ensured by the sufficiently strong interaction between particles.

This concept of the interaction-driven equilibrium is supported by our present results. We have shown that this equilibrium can be described in terms of usual statistical parameters, such as the temperature, even though some of the system's properties are very different from those usually expected in Fermi systems. For example, the statistics of the occupation numbers cannot be described by the Fermi-Dirac formula.

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APPENDIX: DISTRIBUTION OF OCCUPATION NUMBERS FOR A CANONICAL ENSEMBLE OF FINITE SYSTEMS OF INTERACTING FERMIONS

Consider a quantum system which consists of a number of single-particle discrete states α (we will also call them orbitals here) with energies $\varepsilon_\alpha(\alpha=1,\dots,m)$ filled with $n<m$ Fermi particles. The multiparticle states k of the system are identified by specifying the occupation numbers $n_\alpha=0$ or 1 of the orbital α, $\Sigma_\alpha n_\alpha=n$. The total number of multiparticle states $N=\binom{m}{n}$ is quite large, even for moderate m and n. If we allow for the interaction between the particles, the energy of the state k is given by

$$E_k=\sum_\alpha \varepsilon_\alpha n_\alpha+\frac{1}{2}\sum_{\alpha\beta} U_{\alpha\beta}n_\alpha n_\beta, \tag{A1}$$

where $U_{\alpha\beta}$ includes both the direct and exchange interaction between the particles in α and β, and $U_{\alpha\alpha}=0$.

Of course, the states k are not eigenstates of the system. However, if the interaction between the particles is not too strong, we can use them for averaging over the canonical ensemble with probabilities $w_k=Z^{-1}\exp(-E_k/T)$, where $Z=\Sigma_k\exp(-E_k/T)$ is the partition function, and the sum runs over all N multiparticle states [19]. It will be convenient to show explicitly that the partition function depends on the energies of the orbitals $\varepsilon_1,\dots,\varepsilon_m\equiv\{\varepsilon\}$, number of particles n, and temperature T: $Z\equiv Z(\{\varepsilon\},n,T)$ (and, strictly speaking, on the interactions $U_{\alpha\beta}$, if they are not zero).

Using the canonical probabilities we can express the mean occupancy of the orbital α as

$$\overline{n}_\alpha=\sum_k n_\alpha^{(k)}w_k=\frac{\sum_k n_\alpha^{(k)}\exp(-E_k/T)}{\sum_k \exp(-E_k/T)} \tag{A2}$$

$$=\frac{\sum_{k(\alpha)}\exp(-E_k/T)}{\sum_{k(\alpha)}\exp(-E_k/T)+\sum_{k(\overline{\alpha})}\exp(-E_k/T)}, \tag{A3}$$

where $n_\alpha^{(k)}=1$ or 0, depending on whether α is occupied or empty in the state k, and we split the sum over k into two sums over the states $k(\alpha)$ where α is occupied, and $k(\overline{\alpha})$, where it is empty.

Let us first consider the case of noninteracting particles ($U_{\alpha\beta}=0$). It is easy to see that the first sum is then equal to $Z(\{\varepsilon\}'_\alpha,n-1,T)\exp(-\varepsilon_\alpha/T)$ and the second one is $Z(\{\varepsilon\}'_\alpha,n,T)$, where $\{\varepsilon\}'_\alpha$ is the set of $m-1$ orbitals obtained by discarding α from $\{\varepsilon\}$. The equation can then be written as

$$\overline{n}_\alpha=\left[1+\frac{Z(\{\varepsilon\}'_\alpha,n,T)}{Z(\{\varepsilon\}_\alpha,n-1,T)}\exp(\varepsilon_\alpha/T)\right]^{-1}. \tag{A4}$$

This equation is very similar to the Fermi-Dirac formula (1), if we introduce the chemical potential μ by

$$\frac{Z(\{\varepsilon\}'_\alpha,n,T)}{Z(\{\varepsilon\}'_\alpha,n-1,T)}\equiv\exp(-\mu/T). \tag{A5}$$

The problem is that this ratio on the left-hand side in fact depends on which orbital α is deleted from the set $\{\varepsilon\}$ to form $\{\varepsilon\}'_\alpha$, and so does the ''chemical potential'' μ. If we write Eq. (A4) for $\overline{n}_\beta$ with $\beta\neq\alpha$, the set $\{\varepsilon\}'_\beta$ will produce a different ratio $Z(\{\varepsilon\}'_\beta,n,T)/Z(\{\varepsilon\}'_\beta,n-1,T)$, and as a result, a different value of μ. However, $\{\varepsilon\}'_\beta$ can be obtained from $\{\varepsilon\}'_\alpha$ by simply moving the orbital energy from ε_β to ε_α. So, the difference between the values of μ for different orbitals can be probed by calculating the derivative of Eq. (A5) with respect to the energy of some orbital β. Using the relation $\overline{n}_\beta=-T\partial Z/\partial\varepsilon_\beta$, valid for noninteracting particles [see Eqs. (A1) and (A2)], we obtain

$$\frac{\partial\mu}{\partial\varepsilon_\beta}=\overline{n_\beta^{(n)}}-\overline{n_\beta^{(n-1)}}, \tag{A6}$$

where $\overline{n_\beta^{(n)}}$ and $\overline{n_\beta^{(n-1)}}$ are the mean occupation numbers for n and $n-1$ particles distributed among the $\{\varepsilon\}'_\alpha$ orbital set. It is obvious that the right-hand side of Eq. (A6) is larger near the Fermi level, $|\varepsilon_\beta-\mu|\lesssim T$, and is almost zero outside this interval. We can estimate that the total difference between the value of μ for orbitals well below the Fermi level and those well above it is

$$\delta\mu=\int(\overline{n_\beta^{(n)}}-\overline{n_\beta^{(n-1)}})d\varepsilon_\beta=d_1\int(\overline{n_\beta^{(n)}}-\overline{n_\beta^{(n-1)}})\frac{d\varepsilon_\beta}{d_1}$$
$$\approx d_1[n-(n-1)]=d_1, \tag{A7}$$

where d_1 is the mean spacing between the single-particle orbitals. Thus in a system with discrete orbital energies the chemical potential can be considered as constant to within $\sim d_1$ accuracy. At finite temperatures the width of the smoothened Fermi-Dirac ''step'' is of the order of T, therefore $\mu=\text{const}$ is valid for $T\gg d_1$ (or for $\mu\gg d_1$). Note that this condition means that the number of orbitals within the Fermi-Dirac ''step'' is large.

For the interacting particles the sum $\Sigma_{k(\alpha)}\exp(-E_k/T)$ which gives rise to $\exp(\varepsilon_\alpha/T)$ in Eq. (A4) can be written as

$$\sum_{k(\alpha)}\exp(-E_k/T)=\sum_{k(\alpha)}\exp\left[-\frac{1}{T}\left(\sum_{\beta\neq\alpha}\varepsilon_\beta n_\beta+\frac{1}{2}\sum_{\beta,\gamma\neq\alpha}U_{\beta\gamma}n_\beta n_\gamma\right)\right]\times\exp\left[-\frac{1}{T}\left(\varepsilon_\alpha+\sum_{\beta\neq\alpha}U_{\alpha\beta}n_\beta\right)\right]. \tag{A8}$$

In this formula the last exponent contains the energy of the particle in α, which depends on the occupancies n_β of the other orbitals. When summation over $k(\alpha)$ is carried out the exponent is averaged over different distributions of $n-1$ particles among all orbitals but α. The result can be presented approximately as

$$Z(\{\varepsilon\}_\alpha, n-1, T)\exp(-\tilde{\varepsilon}_\alpha/T), \tag{A9}$$

where we replaced the averaged exponent by the exponent containing the *quasiparticle* energy,

$$\tilde{\varepsilon}_\alpha = \varepsilon_\alpha + \sum_{\beta\neq\alpha} U_{\alpha\beta}\overline{n_\beta}, \tag{A10}$$

and the mean values $\overline{n_\beta}$ are, strictly speaking, different from those from Eq. (A2), as one particle has always been kept in α in the sum (A8). Therefore the ''Fermi-Dirac'' ansatz (A4) holds for the interacting particles, if we replace the single-particle energies ε_α with the temperature-dependent quasiparticle energies $\tilde{\varepsilon}_\alpha$ from Eq. (A10).

Note that the transformation of Eq. (A8) into Eqs. (A9), (A10) is exact up to first order in $\overline{n_\beta}$, and to all orders, if $U_{\alpha\beta}\equiv U$ for all orbitals. In the latter case $\tilde{\varepsilon}_\alpha = \varepsilon_\alpha + (n-1)U$ is a trivial redefinition of the single-particle energies. That is why replacing ε_α with the quasiparticle energies $\tilde{\varepsilon}_\alpha$ is a valid operation, unless the interactions $U_{\alpha\beta}$ fluctuate strongly, and the number of active particles is small. In the latter case the mean-field approximation is inadequate and the introduction of quasiparticles is not very meaningful.

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[1] V. V. Flambaum, A. A. Gribakina, G. F. Gribakin, and M. G. Kozlov, Phys. Rev. A **50**, 267 (1994); A. A. Gribakina, V. V. Flambaum, and G. F. Gribakin, Phys. Rev. E **52**, 5667 (1995).

[2] M. Horoi, V. Zelevinsky, and B. A. Brown, Phys. Rev. Lett. **74**, 5194 (1995); Phys. Lett. B **350**, 141 (1995); V. Zelevinsky, B. A. Brown, N. Frazier, and M. Horoi, Phys. Rep. **276**, 85 (1996).

[3] V. V. Flambaum, F. M. Izrailev, and G. Casati, Phys. Rev. A **54**, 2136 (1996).

[4] V. V. Flambaum and F. M. Izrailev, Phys. Rev. E **55**, R13 (1997); **56**, 5144 (1997).

[5] D. Pines and P. Noziéres, *The Theory of Fermi Liquids* (Benjamin, New York, 1966).

[6] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, New York, 1969).

[7] W. C. Martin, R. Zabulas, and L. Hagan, *Atomic Energy Levels—The Rare-Earth Elements*, Natl. Bur. Stand. (U.S.) Natl. Bur. Stand. Ref. Data Ser. No. NBS-60 (U.S. GPO, Washington, DC, 1978).

[8] V. V. Flambaum, A. A. Gribakina, and G. F. Gribakin, Phys. Rev. A **54**, 2066 (1996).

[9] Of course, if one needs good qualitative results for the spectrum of Ce, virtual core excitations must be taken into account. This can be done, for instance, by introducing the effective correlational electron-core potential and the screened Coulomb interaction between the valence electrons using many-body theory methods, V. A. Dzuba, V. V. Flambaum, and M. G. Kozlov, Phys. Rev. A **54**, 3948 (1996).

[10] A. Bohr and B. Mottelson, *Nuclear Structure* (Benjamin, New York, 1969), Vol. 1.

[11] It is known that the level density in the n-particle system with k-body interaction becomes Gaussian for $n\gg k$, see J. B. French and S. S. M. Wong, Phys. Lett. **35B**, 5 (1970); O. Bohigas and J. Flores, *ibid.* **34B**, 261 (1971).

[12] This analogy was clearly stated by V. V. Flambaum and O. K. Vorov, Phys. Rev. Lett. **70**, 4051 (1993).

[13] E. P. Wigner, Ann. Math. **62**, 548 (1955); **65**, 203 (1957).

[14] Y. V. Fyodorov, O. A. Chubykalo, F. M. Izrailev, and G. Casati, Phys. Rev. Lett. **76**, 1603 (1996).

[15] B. L. Altshuller, Y. Gefen, A. Kamenev, and L. S. Levitov, Phys. Rev. Lett. **78**, 2803 (1997); A. D. Mirlin and Y. V. Fyodorov, Phys. Rev. B **56**, 13 393 (1997).

[16] P. Jacquod and D. L. Shepelyansky, Phys. Rev. Lett. **79**, 1837 (1997); D. L. Shepelyansky and O. P. Sushkov, Europhys. Lett. **37**, 121 (1997); B. Georgeot and D. L. Shepelyansky, , Phys. Rev. Lett. **79**, 4365 (1997).

[17] P. G. Silvestrov, Phys. Rev. Lett. **79**, 3994 (1997); cond-mat/9712036, 1997.

[18] A. B. Migdal, *Theory of Finite Fermi-Systems, and Applications to Atomic Nuclei* (Interscience, New York, 1967).

[19] The eigenstates of the system are in fact linear combinations of the states k, which can be considered as multiparticle basis states of the system in the Fock space. The mixing of these basis states within the eigenstates occurs *locally*, in the energy interval determined by the spreading width Γ, which depends on the strength of the residual interaction between the particles and practically does not depend on energy. It is usually narrower than the typical interval involved in averaging over the canonical ensemble, which increases as $T^{3/2}$ [this estimate follows from Eq. (8)].

[20] In numerical calculation we always have to cut off the Hamiltonian matrix somewhere. Therefore we call the exact states here the eigenstates of the matrix in the truncated basis.