Can we apply statistical laws to small systems?

The cerium atom.

I. V. Ponomarev, V. V. Flambaum, A. A. Gribakina and G. F. Gribakin
School of Physics, The University of New South Wales, Sydney 2052, Australia

It is shown that statistical mechanics is applicable to quantum systems with finite numbers of particles, such as complex atoms, atomic clusters, etc., where the residual two-body interaction is sufficiently strong. This interaction mixes the unperturbed shell-model basis states and produces “chaotic” many-body eigenstates. As a result, an interaction-induced equilibrium emerges in the system, and temperature can be introduced. However, the interaction between the particles and their finite number can lead to prominent deviations of the equilibrium occupation numbers distribution from the Fermi-Dirac shape. For example, this takes place in the cerium atom with four valence electrons, which was used to compare the theory with realistic numerical calculations.

1. Introduction. Statistical behaviour is usually established in the limit of a large number of particles \( n \). Moreover, quantitative results can be obtained if correlations between the particles are somehow weak. This means that the interaction between the particles is to be neglected, or, a more realistic possibility, an appropriate mean field theory is chosen. The latter results in the picture of free quasiparticles moving in the effective self-consistent field created by the constituents.

In this limit the temperature \( T \) is a well-defined physical quantity and all equilibrium characteristics can be found. For example, for a gas of noninteracting fermions this results in the famous Fermi-Dirac distribution (FDD) of the occupation numbers: \( \pi_\alpha = 1/(\exp[(\varepsilon_\alpha - \mu)/T] + 1) \). There are many real complex systems, such as compound nuclei, rare-earth atoms, molecules, quantum dots, etc., which do not satisfy the conditions for FDD to hold. The number of active particles in these systems can be relatively small (~10), and the interaction between them (even the residual interaction in the mean-field basis) is large, i.e., greater than the energy intervals between unperturbed basis states. However, this interaction makes up for the absence of a heat bath, and promotes the onset of “randomization” and quantum chaos, which 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.

2. The Ce atom. The cerium atom has one of the most complicated spectra in the periodic table. Its electronic structure consists of a Xe-like \( 1s^2 \ldots 5p^6 \) 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 form the spectrum of Ce below the ionization threshold.

The calculations are performed using the Hartree-Fock-Dirac (HFD) and configuration interaction (CI) methods (see[1] for details). A self-consistent HFD calculation determines the mean-field potential, which is then used to calculate the basis set of single-particle ortho-normalized relativistic states \( |\alpha\rangle = |njjz\rangle \) with energies \( \varepsilon_\alpha \). This procedure defines the zeroth-order Hamiltonian of the system, \( \hat{H}^{(0)} = \sum_\alpha \varepsilon_\alpha a_\alpha^\dagger a_\alpha \). The unperturbed multi-particle 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 \( \hat{H}^{(0)} \): \( \hat{H}^{(0)} |k\rangle = \varepsilon_k |k\rangle \).

\[ \text{[1]} \]
\[ E_k^{(0)} |k\rangle, \text{where } E_k^{(0)} = \sum_\alpha \varepsilon_\alpha n_\alpha^{(k)} \text{ and } n_\alpha^{(k)} = \langle k | a_\alpha^\dagger a_\alpha |k\rangle \text{ are the occupation numbers equal to } 0 \text{ or } 1. \]

The total Hamiltonian \( \hat{H} \) of the active electrons is the sum of the zeroth-order mean-field Hamiltonian \( \hat{H}^{(0)} \) and the 2-body residual interaction
\[ \hat{V} = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} V_{\alpha\beta\gamma\delta} a_\alpha^\dagger a_\beta^\dagger a_\gamma a_\delta. \]

This interaction contributes to the diagonal and off-diagonal matrix elements between the multi-particle states \(|k\rangle\). The diagonal part represents an additional energy shift of the state \(k\), and can still be expressed in terms of the occupation numbers. The off-diagonal matrix elements are responsible for mixing of the multi-particle basis states.

Complete diagonalization of the operator \( \hat{H} = \hat{H}_d + \hat{V} \) within the space of the \(|k\rangle\) basis states produces “exact” energies \(E_i\) and stationary states \(|i\rangle\):

\[ \hat{H} |i\rangle = E_i |i\rangle, \quad |i\rangle = \sum_k C_k^{(i)} |k\rangle. \tag{1} \]

We included 14 relativistic subshells \(nlj\) in the calculation (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. To subtract additional symmetries our numerical results are obtained for the even states of Ce with the total angular momentum projection set to \(J_z = 0\).

The relativistic atomic subshells \(nlj\) are \(g_s = 2j + 1\) degenerate, therefore, we consider average occupation numbers for the subshells \(s\): \(\bar{n}_s = g_s^{-1} \sum_{\alpha \in s} a_\alpha^\dagger a_\alpha\). When the number of active particles is small, the occupation numbers for any eigenstate \(n_s^{(i)} = \langle i | \bar{n}_s | i \rangle\) show strong level-to-level fluctuations, and it is more instructive to look at spectrally averaged values

\[ n_s(E) = \overline{\langle i | \bar{n}_s | i \rangle} = \sum_k |C_k^{(i)}|^2 \langle k | \bar{n}_s | k \rangle, \tag{2} \]

where the overline means averaging over the eigenstates \(i\) within some energy interval around energy \(E\).

A typical distribution of the occupation numbers calculated at the excitation energy of 3.75 eV above the atomic ground state is shown in Fig. 1 as a function of the single-particle energy \(\varepsilon_s\) of the orbitals. One can see that the distribution does not look at all like a monotonically decreasing FDD, as some higher-energy orbitals have larger \(n_s(E)\) than the lower ones. Moreover, this behaviour persists 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 \(4f^26s^2\), while the FDD would tell us that all 4 electrons must be placed in the lowest 4\( f\)-orbital, when the energy of the system is low. At first sight such a strong deviation from the FDD in a strongly interacting Fermi system speaks against any possibility of statistical description of the system. However, we show that strongly interacting orbitals can be properly incorporated in the canonical ensemble description of the system, and thermally averaged occupation numbers \(n_s(T)\) derived.

3. **Statistical model.** Let us perform a statistical calculation of the occupation numbers for a system of \(n\) particles distributed over \(r\) orbitals with energies \(\varepsilon_s\) 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:

$$U_{sp} = \frac{1}{g_s(g_p - \delta_{sp})} \sum_{\alpha \in s} \sum_{\beta \in p} (V_{\alpha\beta\beta\alpha} - V_{\alpha\beta\alpha\beta}).$$  \hspace{1cm} (3)$$

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

$$E_k = \sum_{s=1}^{r} N_s \varepsilon_s + \sum_{s=1}^{r} \sum_{p=s}^{r} \frac{N_s (N_p - \delta_{sp})}{1 + \delta_{sp}} U_{sp},$$  \hspace{1cm} (4)$$

where $N_s$ is an integer number of particles in the orbital $s$ ($0 \leq N_s \leq g_s$), and $\sum_s N_s = n$. The state $k$ is defined by specifying the orbital occupation numbers $N_s$, and is $G_k$-degenerate, where $G_k = \prod_{s=1}^{r} \left( \frac{g_s}{N_s} \right)$.

In the canonical ensemble at temperature $T$ the probability of finding the system in the state $k$ is given by

$$w_k = Z^{-1} G_k \exp(-E_k/T), \quad \text{where} \quad Z = \sum_k G_k \exp(-E_k/T) \hspace{1cm} (5)$$

and the sum over $k$ runs over all possible multi-particle states (possibly, with the restriction of parity). The average occupation numbers $n_s(T) = \overline{N_s}/g_s$ are calculated as

$$n_s(T) = g_s^{-1} \sum_k N_s^{(k)} w_k,$$  \hspace{1cm} (6)$$

where $N_s^{(k)}$ is the number of particles in the orbital $s$ in the multi-particle state $k$. The energy of the system at a given temperature is $\overline{E}(T) = \sum_k E_k w_k$. If we know $\overline{E}(T)$, we can find inverse function $T(\overline{E})$ and use it in (6) in order to compare with the data from (2). This comparison is shown in figure 2 and good agreement is observed.

4. Discussion. This agreement means that a kind of equilibrium is indeed induced in the system due to the interaction between the particles (“micro-canonical” distribution). Moreover, the averaging over it yields results close to those over a canonical ensemble (5), with the temperature chosen to reproduce the total energy of the system. This equivalence is always true for large systems where any, albeit weak, interaction between particles leads to equilibrium. However, in a few-particle system the residual two-body interaction must be strong to produce chaotic eigenstates and facilitate statistical description.
Figure 2: Comparison of the orbital occupancies $g_s n_s(E)$ obtained from the exact diagonalization (solid and dash-dot lines) with $g_s n_s(T(E))$ obtained from our statistical theory (dotted lines).

Note, that although the temperature-based description is valid for our 4-particle system, the orbital occupancies could not be described by the FDD (Fig. 1). The FDD is inapplicable to our system because of the strong interaction between the particles [second term on the the right-hand side of Eq. (4)]. 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 $U_{sp} \equiv U$ are the same. In this case the double sum in Eq. (4) just shifts all energies by $U^2 N(N - 1)$, and the statistical properties of the system are the same as for noninteracting particles. If $U_{sp}$ are different for different orbital pairs $sp$ one can still introduce some average interaction $\bar{U}$ and subtract this “background” interaction from the interaction term in Eq. (4). This procedure will effectively suppress the interaction term, since the summands in expressions like $\sum_{s<p} (U_{sp} - \bar{U}) N_p$ have different signs. Note that the introduction of (energy-dependent) $\bar{U}$ is equivalent to a mean-field approximation. This approximation is good if the fluctuations of $U_{sp}$ from one orbital to another are relatively small. This formulates a condition for the FDD to be valid. In the Ce atom the situation is just opposite. The $4f$ orbital has a much smaller radius than any other orbital, hence the Coulomb interactions $U_{4f4f}$ or $U_{4fs}$ are much greater than any other $U_{sp}$ (here $s$ and $p$ are orbitals other than $4f$).

References

[a] e-mail: ilya@newt.phys.unsw.edu.au
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4. Of course, when this interaction is strong one needs to introduce some new mean-field orbital energies $\tilde{\epsilon}_s$ that would incorporate the effect of such interaction. The value $\tilde{\epsilon}_s$ will inevitably depend on the distribution of the other electrons, and hence on the excitation energy of the system. However, even when $\tilde{\epsilon}_s$ are used there is a noticeable deviation from the simple FDD distribution.