Decay of a condensate consisting of excited cesium atoms

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The main recombination channels for the condensed excited state (Rydberg matter) consisting of highly excited cesium atoms are investigated theoretically. The density functional theory with the concept of a pseudopotential and the method of spherical cells are employed. The recombination time increases rapidly for high excitation levels, but the dependence is sharply nonmonotonic. The decay proceeds, as a rule, by the Auger recombination mechanism.

INTRODUCTION

Condensed excited states (CES) arise in dense systems of excited atoms, molecules, and impurity centers in solids.[1] The behavior of such systems changes qualitatively at densities at which the wave functions of the valence electrons of the excited centers overlap appreciably. The condensed state in which valence electrons are collectivized as in alkali metals turns out to be energetically most favorable. Numerical estimates show that CES are quite stable formations even for strongly excited atoms. For example, the binding energy of atoms in the condensate is an appreciable fraction of the initial kinetic energy of the electrons.

Condensed excited states are inherently unstable and have a finite lifetime. At first glance, the lifetime of excitations in a condensate should be shorter than for isolated excited centers. The strong Coulomb interaction of the electrons promotes this. It is shown in Ref. 2 that the lifetime of the condensate can, under certain conditions, increase significantly, thanks to the existence of collective confinement of Auger electrons. As the excitation level increases, however, the lifetime of CES can be expected to increase rapidly in connection with the spatial separation of the initial and final states of the electrons and specific effects of the local field in the strongly nonuniform electron liquid of the condensate. The higher the level of excitation, the more strongly the electrons are drawn to the boundaries of the unit cells. In this case, the final states remain localized near the ionic cores. Due to energy shifts, recombination cannot occur into all lower-lying states of the isolated atom. As a result of this, for CES consisting of highly excited atoms (Rydberg matter) the lifetime can, apparently, be infinite.[3]

One possible method for detecting CES is to observe the recombination spectrum. In so doing, it is important to assess how much the spectrum and intensity of the recombination radiation change, taking into account the qualitative restructuring of the system.

The behavior of a dense system of excited cesium atoms was recently investigated experimentally.[4,5] In Ref. 4, clusters of excited cesium atoms, containing on the order of 10^4 atoms, were observed by means of time-of-flight mass spectrometry. In Ref. 5 the current-voltage characteristic of the gap, probably containing a condensate consisting of excited cesium atoms, was measured. It was found that there exists an ohmic resistance and the resistivity of the condensate was estimated. In this connection, it is of interest to obtain a quantitative estimate of the lifetime of the observed CES.

In the present paper we find the main recombination channels and estimate the lifetimes and characteristic parameters of the recombination radiation for CES consisting of highly excited cesium atoms. It is shown that as the excitation level increases the lifetime increases rapidly, and it exceeds 10 h even for a condensate consisting of atoms excited into the 15S state. The recombination of excitation proceeds, as a rule, by the Auger mechanism.

In order to describe CES we employ the density functional theory combined with the concept of a pseudopotential. The local density approximation is employed in the method of spherical cells.

DECAY STATES

The potential W acting on a valence electron within a Wigner–Seitz unit cell of the condensate consists of the Coulomb potential v_i of the ionic core, the Hartree potential v_H, and the effective exchange-correlation interaction potential v_{xc}. For CES consisting of highly excited atoms, the collectivized valence electrons are distributed very nonuniformly over the cell: The density of the electron liquid differs appreciably from zero only near the cell boundaries. If the electron distribution over the cell is described by a one-parameter function with a Gaussian profile

$$\rho(r) = \rho_0 \exp[(r - R_{WS})^2/D^2],$$

where $R_{WS} = R_n + D$ is the cell radius and R_n is the radius of the Aschcroft pseudopotential of the corresponding nth state of the excited atom, then the optimal distribution width is found to be $D \approx 1.8 R_n^{0.4}$ (Ref. 1). Since the radius of the pseudopotential increases approximately as n^2 with increasing excitation level, the parameter $\mu = D/R_n$, characterizing the nonuniformity of the distribution, decreases rapidly with increasing n. Indeed, the tendency for the nonuniformity of the electron charge distribution to increase is also observed in atoms: As the excitation level increases, the Bohr radius increases as n^2 and the de Broglie wavelength increases only as n. As a result of this, the Hartree potential within the cell is constant almost everywhere and decreases somewhat only near the boundary of the cell at distances of the order of D. The Hartree potential at the boundary is identical to the Coulomb potential, since the cells are electrically neutral. In the local approximation the effective exchange-correlation interaction potential differs from the Slater exchange potential only by a numerical factor $v_{xc} = -1.93\rho^{1/3}$. In the region of low-lying internal shells, the potential v_{xc} is practically zero. Thus the internal recombination states of the excited atoms in the condensate are shifted upwards by a constant amount, approximately equal to the average value of the Hartree potential: $I^c_{n,l} = I_{n,l}$
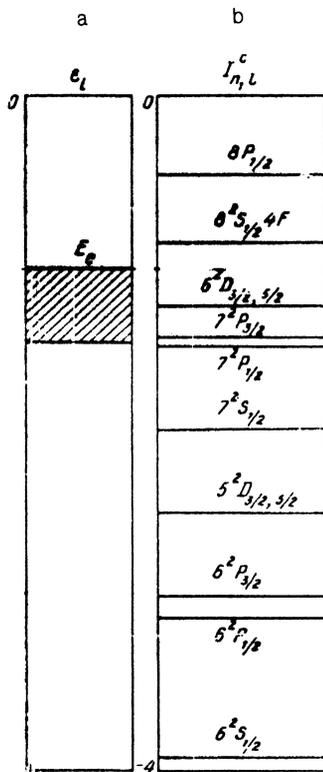
FIG. 1. Initial (a) and final (b) states of recombination for a condensate consisting of excited cesium atoms (10S).

$+ U_H$, where $I_{n,l}$ are the term values for an isolated atom.

Compared with the states of isolated atoms, the initial states are shifted downwards, since the CES are energetically favorable. In order to determine the position of the average energy level E_e of the electrons in CES (or the Fermi level E_F), we employ the narrowness of the conduction band of the condensate in energy space, i.e., the small parameter $\max\{|(\varepsilon_i - \varepsilon_j)/\varepsilon_i|\} < 1$, where ε_i are the eigenvalues of the Kohn–Sham equation. It is well known from the density-functional theory that

$$\sum_i \varepsilon_i = E + E_H - E_{xc} - \int dr\rho(\mathbf{r}) v_{xc},$$

where E is the energy of the electrons in the condensate, E_H is the Hartree potential, and E_{xc} is the exchange-correlation

contribution to the energy of the electrons. Taking into account the narrowness of the bands, $\Sigma \varepsilon_i \approx NE_e$, whence we find $E_e \approx (E + E_H + E_{xc}/3)/N$, where N is the number of electrons.

The energetically allowed decay states are determined by the condition

$$I_{n,l} + U_H < E_e. \tag{1}$$

Using the known term values of the cesium atom $I_{n,l}$ (Ref. 6), we can find all the energetically allowed decay states. Figure 1 shows the relative position of the energy levels of the electrons in CES consisting of cesium atoms excited into the 10S state. One can see that spontaneous decay for this condensate is possible only into a state with principal quantum number $n_f \leqslant 7$. Thus it is also possible to study CES consisting of very highly excited states. Table I gives the energetically allowed decay states for a condensate consisting of cesium atoms excited into the nS state, where $n = 10$, ..., 16. As the excitation level increases, the difference between the quantum number n of the initial state and the quantum number n_f of the final state increases.

DECAY PROBABILITY

In order to determine the probability of decay via one or another mechanism, it is necessary to know the wave functions of the initial and final states.

The initial states of the electrons in CES differ significantly from atomic states. In addition, the electron liquid is pressed toward the boundaries of the unit cells by the exchange-correlation interaction. This effect is described quantitatively by the effective exchange-correlation potential v_{xc}. In a system with an undeformed compensating background this interaction results in charge-density waves.[7] For a neutralizing system in the form of ions, effective trapping of electrons near the cell boundaries is possible if a non-Coulombic correction is present in the electron-ion interaction potential.[8] The non-Coulombic part of the electron-ion interaction appears as a result of orthogonalization of the wave function of the valence electrons to the lower-lying states. Trapping is possible, if the radius of the pseudopotential, characterizing the non-Coulombic correction, satisfies the condition $R_n > 20$–30.

As we have already noted, the final decay states differ to

TABLE I.

Excitation level	Decay state
10	$6^2S_{1/2}$, $6^2P_{1/2}$, $6^2P_{3/2}$, $5^2D_{3/2}$, $5^2D_{5/2}$, $7^2S_{1/2}$, $7^2P_{1/2}$, $7^2P_{3/2}$, $6^2D_{3/2}$, $6^2D_{5/2}$.
11	$6^2S_{1/2}$, $6^2P_{1/2}$, $6^2P_{3/2}$, $5^2D_{3/2}$, $5^2D_{5/2}$, $7^2S_{1/2}$, $7^2P_{1/2}$, $7^2P_{3/2}$, $6^2D_{3/2}$, $6^2D_{5/2}$, $8^2S_{1/2}$, $4^2F_{5/2}$, $4^2F_{7/2}$, $8^2P_{1/2}$.
12	$6^2S_{1/2}$, $6^2P_{1/2}$, $6^2P_{3/2}$, $5^2D_{3/2}$, $5^2D_{5/2}$, $7^2S_{1/2}$, $7^2P_{1/2}$, $7^2P_{3/2}$, $6^2D_{3/2}$, $6^2D_{5/2}$, $8^2S_{1/2}$, $4^2F_{5/2}$, $4^2F_{7/2}$, $8^2P_{1/2}$, $8^2P_{1/2}$, $8^2P_{3/2}$, $7^2D_{3/2}$, $7^2D_{5/2}$.
13	$6^2S_{1/2}$, $6^2P_{1/2}$, $6^2P_{3/2}$, $5^2D_{3/2}$, $5^2D_{5/2}$, $7^2S_{1/2}$, $7^2P_{1/2}$, $7^2P_{3/2}$, $6^2D_{3/2}$, $6^2D_{5/2}$, $8^2S_{1/2}$, $4^2F_{5/2}$, $4^2F_{7/2}$, $8^2P_{1/2}$, $8^2P_{1/2}$, $8^2P_{3/2}$, $7^2D_{3/2}$, $7^2D_{5/2}$, $9^2S_{1/2}$, $5^2F_{5/2}$, $5^2F_{7/2}$, $5^2G_{7/2}$, $5^2G_{9/2}$.
14	$6^2S_{1/2}$, $6^2P_{1/2}$, $6^2P_{3/2}$, $5^2D_{3/2}$, $5^2D_{5/2}$, $7^2S_{1/2}$, $7^2P_{1/2}$, $7^2P_{3/2}$, $6^2D_{3/2}$, $6^2D_{5/2}$, $8^2S_{1/2}$, $4^2F_{5/2}$, $4^2F_{7/2}$, $8^2P_{1/2}$, $8^2P_{1/2}$, $8^2P_{3/2}$, $7^2D_{3/2}$, $7^2D_{5/2}$, $9_2S_{1/2}$, $5^2F_{5/2}$, $5^2F_{7/2}$, $5^2G_{7/2}$, $5^2G_{9/2}$, $9^2P_{1/2}$, $9^2P_{3/2}$, $8^2D_{3/2}$, $8^2D_{5/2}$.
15,16	Transitions into the state $n_f = 10$ are added.

TABLE II.

Excitation level n	Most likely decay state	Transition energy, eV	Broadening, eV	Probability (sec^{-1}) of decay	
				by radiative mechanism	by Auger mechanism
10	$7^2S_{1/2}$	0.6	0.2	11	650
11	$8^2S_{1/2}$	0.14	0.18	2.5	1540
12	$8^2S_{1/2}$	0.29	0.14	$3 \cdot 10^{-3}$	0.04
13	$9^2S_{1/2}$	0.1	0.1	$2 \cdot 10^{-3}$	0.2
14	$9^2S_{1/2}$	0.16	0.08	$6 \cdot 10^{-7}$	$3.5 \cdot 10^{-6}$
15	$10^2S_{1/2}$	0.03	0.06	$1.3 \cdot 10^{-7}$	$2.7 \cdot 10^{-5}$
16	$10^2S_{1/2}$	0.07	0.05	$4 \cdot 10^{-11}$	$2.9 \cdot 10^{-10}$

first approximation from the states of the isolated atom by a constant shift U_H. In addition, the highly excited states of the atom are hydrogen-like. Far from the atomic core the wave functions are Coulombic, and the difference of the spectrum from the hydrogen atom is taken into account with the help of the quantum defect. For cesium (S state) the quantum defect is $\delta \approx 4$ (Ref. 9).

Localization of the initial states near the boundaries of large unit cells significantly simplifies the problem of estimating the decay probability.[3] It is convenient to represent the wave function of the electrons of the CES in the form $\psi = A \exp[g(r)]$, where the function $g(r)$ has a sharp maximum near the boundaries of the unit cells. In the approximation of intracell transitions the probability of radiative decay is determined by the expression

$$w_i \approx \frac{4\hbar^3\omega^3 I_r^2}{3m^2e^2c^3}. \tag{2}$$

where $\omega = (E_e - I_{nl})/\hbar$ is the transition frequency and I_r is the overlap integral of the initial and final states.[3] The overlap integral simplifies significantly, if the function $g(r)$ is expanded near its maximum:

$$g(r) \approx \alpha + \beta(r - R_{ws}) + \gamma(r - R_{ws})^2 + \ldots . \tag{3}$$

where $\alpha = 0, \beta = 0$, and $\gamma = -1/2D^2$. In this case

$$I_r \approx B_f^{\,f+2}D^{0.5}R_0^{-1}a_0^{\,f+1.5}$$

$$\times \exp[\gamma(R_f - R_0)(R_f + R_0 - 2R_{ws}) - R_f/fa_0],$$

where

$$R_f = R_{ws} - D[D/fa_0 - D(f+2)/(R_{ws} - D^2/fa_0)],$$
$$R_0 = R_{ws} + D^2/R_{ws}, \quad B_f = 2^f/f^{f+1}[(f+1)!(f-2)!]^{0.5},$$

$f = (n_f - \delta)$ and a_0 is the Bohr radius. The probability of Auger decay can be determined approximately by the expression

$$w_0 \approx 0.01 \frac{me^4}{\hbar^3}\left(\frac{D}{R_{ws}}\right)^6 I_0^2, \tag{4}$$

where the overlap integral has the form

$$I_0 \approx b_f r_f^{\,f+1} D^{0.5}R_0^{-1}a_0^{-f-0.5}\exp[\gamma(r_f - R_0)(r_f + R_0 - 2R_{ws}) - r_f/fa_0],$$

$$b_f = 2^f/f^{f+1}[f!(f-1)]^{0.5},$$

$$r_f = R_{ws} - D[D/fa_0 - D(f+1)/(R_{ws} - D^2/fa_0)].$$

The overlap integrals contain the factor $\exp(-R_{ws}/fa_0)$, so that transitions into a state of the atom with maximum possible principal quantum number n_f are most likely (see Table I). Transitions into an atomic state with smaller

values of the principal quantum number are exponentially suppressed.

Table II gives the decay probabilities of CES consisting of excited cesium atoms by the radiative recombination and Auger mechanisms. The table also gives estimated values of the transition energies $E_e - I_{nl}$ and the band broadening of the lines ΔE. The line broadening due to the finite width of the conduction band of the CES can be estimated according to the formula $\Delta E = E_e - W(R_{ws})$, where the value of the intracell effective potential at the boundary of the cell is taken as the bottom of the band.

The nonradiative decay process predominates for all states considered.

CONCLUSIONS

Figure 2 shows the lifetime of CES as a function of the excitation level n of the constituent cesium atoms. The lifetime increases rapidly with n. The increase in the lifetime is nonmonotonic: Sharp drops for $n = 11, 13$, and 15 are observed, superposed on rapid growth. One can see from Tables I and II that for these CES new energetically allowed decay channels open up as n_f increases by unity. The lifetime of CES for excitation levels $n > 12$ is macroscopically long (longer than 5 sec). The real mechanism of decay of the long-lived states can be different. For example, CES can de-
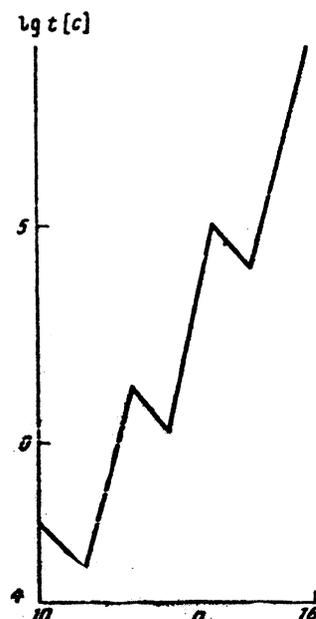
FIG. 2. Lifetime t of the condensate versus the level of excitation of its constituent cesium atoms.

cay by means of thermal evaporation or chemical reactions, in particular, oxidation of cesium. The binding energy of the atoms, i.e., the heat of sublimation at zero temperature, is small in CES. In addition, the condensate of highly excited atoms is quite loose, so that oxygen can penetrate easily into the volume of the condensate.

The characteristic parameters of the recombination radiation accompanying decay of CES are presented in Table II. Of course, these data are only approximate. The probability of nonradiative transitions is one or two order of magnitudes higher than the probability of recombination accompanied by emission. In addition, the probability of transitions into a state of the atom with principal quantum number $n < n_{f,\max}$ is exponentially suppressed. Therefore the main mechanism of decay of CES can be represented as follows: An electron from the conduction band of the condensate passes nonradiatively into an inner orbital of the atom with the maximum possible quantum number n_f. Further relaxation proceeds along the atomic ladder. In addition, since the inner atomic states are practically unchanged (they are all shifted upwards by an amount U_H), the radiation spectrum is indistinguishable from the atomic spectrum. Thus, because the radiation is weak and the spectrum does not differ much from the emission spectrum of excited atoms, it is difficult to detect CES by investigating the recombination spectrum.

The method of measuring some macroscopic parameter of the condensate is probably more promising. Measurements of this kind were performed in Ref. 5. The value 10^{-3} -10^{-2} $\Omega \cdot$ m with a cesium emitter temperature of 800 K and lower was obtained for the resistivity of the condensate. At finite temperature T a condensate for which $|B| > 3kT/2$, where B is the binding energy of the atoms and k is Boltzmann's constant, could be stable. At $T = 800$ K a condensate consisting of cesium atoms excited into states with $n \leqslant 14$ still satisfies this condition. Since in Ref. 5 the measurements were apparently performed under static conditions, n could not be less than 12 (for $n = 11$ the lifetimes are of the order of milliseconds). The resistivity of the condensate can be estimated from the formula $\rho_e \approx mv/\rho e^2 l_e$, where v is the average electron velocity, ρ is the electron density, and l_e is the mean free path, which, taking into account the strong nonuniformity of the electron liquid, can be estimated as $l_e \approx R_{WS}$. For CES consisting of excited cesium atoms with $n = 12$, 13, and 14 we obtain the estimate $\rho_e \approx (0.7 -1.0) \cdot 10^{-3}$ $\Omega \cdot$ m.

[1] É. A. Manykin, M. I. Ozhovan, and P. P. Poluektov, Zh. Eksp. Teor. Fiz. **84**, 442 (1983) [Sov. Phys. JETP **57**, 256 (1983)].

[2] J. S. Zmuidzinas, Phys. Lett. A **120**, 422 (1987).

[3] É. A. Manykin, M. I. Ozhovan, and P. P. Poluéktov, Ukr. Fiz. Zh. **34**, 146 (1989).

[4] C. Aman, J. B. C. Pettersson, and L. Holmlid, Chem. Phys. **147**, 189 (1990).

[5] R. Svensson, L. Holmlid, and L. Lundgren, J. Appl. Phys. **70**, 1489 (1991).

[6] I. K. Kikoin [Ed.], Tables of Physical Quantities [in Russian], Atomizdat, Moscow, 1976.

[7] L. M. Sander, J. H. Rose, and H. B. Shore, Phys. Rev. B **21**, 2739 (1980).

[8] E. A. Manykin, M. I. Ozhovan, and P. P. Poluéktov, Preprint No. 4153/9, Institute of Atomic Energy, Moscow, 1985.

[9] R. Stebbings and F. Dunning [Eds.], Rydberg States of Atoms and Molecules, Cambridge University Press, 1985.

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