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Multiphoton Processes in Systems of Rydberg Atoms

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Abstract—Multiphoton nonlinear effects and Raman processes of Rydberg systems (Rydberg atom gas or Rydberg matter) by intense laser fields are considered. Some experiments and basic elements of quantum theory of Rydberg matter are briefly reviewed. A correlation between experimental data and theoretical description is made.

1. INTRODUCTION

Systems consisting of Rydberg atoms (RAs) attract much attention during the last decade. On the one hand, both a single isolated Rydberg atom and RA clusters are of considerable importance for laser physics and technologies. On the other hand, modern laser physics and technologies provide new opportunities for the experimental investigation of many problems that are of fundamental significance for quantum physics and quantum optics. Some of such studies have been already performed. Among those, we should mention investigations around the borderline between classical and quantum physics [1], analysis of information content and transfer of quantum states [2, 3], and experiments with single atoms and ions (see [4] and references therein).

Creation of a coherent superposition of Rydberg states proved to be very useful for the investigation of the classical limit of quantum mechanics. The spectrum of Rydberg levels is nearly equidistant for large values of the principal quantum number. In this sense, an RA forms the same coherent states as a quantum oscillator. An RA in a strong laser wave or a strong magnetic field is an attractive object for studying quantum systems whose classical analog exhibits a chaotic behavior [5, 6]. Nevertheless, at the moment, there is no satisfactory description of the correspondence between the quasi-classical and purely classical behavior of an RA. However, an attempt was made recently to describe the motion of wave packets consisting of Rydberg states with very large orbital momenta (circular Rydberg wave packets) within the framework of the so-called de Broglie–Bohm pilot wave theory [7].

Modern experimental methods make it possible to produce RA systems with sufficiently high concentrations, when the treatment of such a system as a gas becomes incorrect. Rydberg matter (RM) is usually understood as a system of Rydberg atoms where the mean distance between the atoms is comparable with RA sizes. Due to the collectivization of motion of RA electrons [8], RM is reminiscent, to some extent, of the metal phase of matter with an ultralow gas density [9]. Rydberg matter is a metastable condensed phase of the nonequilibrium state of a medium resulting from decay of a nonideal low-temperature plasma or arising under the laser excitation of atomic, molecular, cluster, or aerosol gas species to Rydberg states. The review [10] provides the description of physical and chemical properties, as well as the main relaxation processes of RM decay. Currently, there are several well-established methods of RM creation. Experimental studies of RM started ten years ago [11].

The most obvious and straightforward technique implies a two-photon excitation of alkaline and alkaline–earth atoms to Rydberg states. Vitrant *et al.* [12] made the first attempt to ensure conditions meeting the requirements of Mott phase transition in an RA gas. Rydberg atoms with principal quantum numbers $n = 30$–45 were produced in a laser-pumped cesium vapor. In accordance with the Mott criterion, the phase transition to the metallized state was expected for RA concentrations corresponding to the close packing of RAs, i.e., for RA concentrations meeting the inequality $N_{Cs}(n^2 a_{Br})^3 \geq 1$, where N_{Cs} is the concentration of Cs atoms excited to the nth Rydberg state. Hence, we see that the critical concentration N_{Cs} scales as n^{-6}, while more accurate estimates predicted that the transition to the metal phase should be observed even with the ratio of the mean interatomic distance to the atom size equal to three. The experimentally measured dependence scaled as n^{-4}. Subsequent studies have shown that, for mean distances between cesium RAs no less than 15 times the RA size, an RA gas rapidly decays in an avalanche-like fashion through a long series of sequential chemical reactions involving the formation of various neutral and charged molecular complexes. There-

fore, the required concentrations were not achieved with the use of this method, and no RM was produced. The authors of [12] argued that RM could be created by considerably reducing the influence of relative RA motion, which could be done, for example, by substantially lowering the temperature (below $T = 1$ K) or by drastically decreasing time intervals of RA generation and detection (down to the picosecond scale).

It was found out, however, that mixtures of different sorts of RAs (the so-called RM alloys) can be produced in a rather simple way by using thermal-emission diodes. These methods were thoroughly investigated in a series of studies by Holmlid and his colleagues (see [13] and references therein). This group of researchers developed a method allowing the generation of high concentrations of RAs using special graphite membranes as cathodes in thermal-emission diodes. Cesium gas passing through the pores of a membrane heated with IR laser radiation up to temperatures $T = 1450°C$ was transformed into a mixture of a low-temperature nonideal plasma and a gas consisting of different sorts of RAs. This approach allowed the necessary RA concentrations to be achieved, permitting the conditions required for the condensation of RAs into RM to be provided.

The general theory of condensed excited states (CES), which was developed earlier in [9], was applied to a specific gas of cesium RAs [14], and the theory describing the decay of RM through different relaxation channels (involving spontaneous emission and Auger processes) was developed [15, 16].

An "optical lattice" consisting of cold RAs trapped in a periodic potential [17] is another interesting RA system, which is intensely studied at the moment. Atoms in an optical lattice possess an evident flexibility and can be employed for the generation of quantum states and subsequent control of quantum states [18], as well as for quantum computations [19]. Such RA systems substantially increase their efficiency due to the large number of Rydberg states and, which is even more important, due to large decoherence times attainable in RAs.

We should note also that a considerable progress has been achieved recently in the generation of strongly cooled neutral plasmas, including ultralow-temperature plasmas [20–23] and plasmas allowing RA formation [24–26].

We should specially mention unique experiments on the formation of an ultracold plasma [23, 26]. The decay of such a plasma is one of the possible ways to produce RM. An ultracold neutral plasma with the mean electron density on the order of $n_e = 10^9$ cm^{-3} was created through the photoionization of Xe atoms with the density $n_a = 10^{10}$ cm^{-3} cooled with laser radiation down to ultralow temperatures ($T_e = 100$ mK, $T_a = 10$ μK). Three-body recombination is suppressed with

such plasma parameters, and the kinetic (thermal) energy of plasma species is lower than the mean Coulomb energy, which makes the plasma a strongly Coulomb-coupled system. Xenon atoms were excited to a metastable state (with a lifetime of 43 s) for laser cooling through the transition with $\lambda_1 = 882$ nm with subsequent trapping in a magneto-optical trap with the size $d \approx 200$ μm. About 10^6 atoms were trapped in this trap. Two-photon ionization at $\lambda_2 = 514$ nm (the green beam) was employed for this purpose. The difference Δ between the final level of photoelectron excitation and the ionization potential of Xe was varied within the range of $\Delta/k = 0.1–1000$ K by changing the frequency of the green beam. The lower limit was imposed by the bandwidth of this beam (0.007 cm^{-1}). Thus, the initial velocity of a photoelectron was $v = \{2\Delta/m\}^{1/2}$. The number of photoions was controlled by changing the energy of laser pulses. The maximum value of this energy was 1 mJ per 10-ns pulse, which allowed up to 2×10^5 ions to be produced. The Debye screening length, $l = \{kT/4\pi e^2 n_e\}^{1/2}$, could reach the minimum value $l \approx 500$ nm, which implies that the condition of plasma formation is satisfied, i.e., $l < d$. The opposite inequality, $l > d$, is characteristic of the ionized-gas phase, rather than the plasma phase. The equality $l = d$ determines the critical concentration of the phase transition. Killian et al. [23] argued that the energy of a trapped electron in the gas phase is completely transformed into the kinetic energy in the plasma, with $T_e \leq \Delta/k$, when the system passes through the critical point, and the above-specified values of T_e and T_a are achieved as a result of the thermalization process. It can be easily seen that the conditions of RM formation are realized when the inequality $\Delta < 0$ is met. In this case, a dense gas of highly excited supercooled RAs characterized by a considerable overlapping of electron shells may be produced. Consequently, a Mott transition to a metallized or another plasma-like state may occur under much more favorable conditions than the conditions attained in the above-described situation. Many-body quantum interactions become important in this regime, prevailing over elastic and inelastic collisions in gas phases. Killian et al. [26] studied RA formation in an expanding plasma with a temperature varying within the range of 1–1000 K and densities of $10^5–10^{10}$ cm^{-3}. It was found that up to 20% of the initial charges recombine within approximately 100 μs. This rather long lifetime is inconsistent with the mechanism of three-body recombination. The energy of RA coupling is approximately equal to the kinetic energy of free electrons surviving through the recombination. Thus, the conditions implemented in these experiments not only allow the formation of a large number of RAs in an ultracold neutral plasma, but also permit RM formation.

Summarizing the aforesaid, we should note that, on the one hand, RM exhibits many properties characteris-

tic of metals. On the other hand, several unusual properties are observed in this case. For example, the density of RM corresponds to rarefied gases, RM is transparent in the optical range, possesses a high plasticity and a sufficiently high coefficient of surface tension, which allows the formation of a sharp boundary between an RM and gas media.

In this paper, we provide theoretical estimates for the nonlinear-optical properties of RAs and RA systems, including RM, responsible for multiphoton processes. We will demonstrate that the linear and nonlinear susceptibilities for RAs and RM are rather high as compared with typical linear and nonlinear susceptibilities of ground-state atoms. This conclusion is confirmed by the results of experiments devoted to the observation of Raman scattering, four-wave mixing, and multiphoton photoionization. We will then provide a brief review of some of the RM properties. Theoretical results will be compared with the results of recent experiments.

2. NONLINEAR SUSCEPTIBILITIES OF A RAREFIED GAS OF RYDBERG ATOMS

We will illustrate our method of estimating nonlinear susceptibilities and specify our main approximation by estimating linear susceptibilities.

The well-known formula for the linear susceptibility $\chi_{\alpha\beta}^{(1)}(\omega)$ of an arbitrary quantum-mechanical system residing in some stationary state $|i\rangle$ can be represented as

$$\chi_{\alpha\beta}^{(1)}(\omega) = N\sum_m \left\{ \frac{d_{im}^{(\alpha)}d_{mi}^{(\beta)}}{\hbar\omega + \hbar\omega_{mi}} - \frac{d_{im}^{(\beta)}d_{mi}^{(\alpha)}}{\hbar\omega - \hbar\omega_{mi}} \right\}, \quad (1)$$

where $d_{mi}^{(\alpha)}$ and $d_{im}^{(\beta)}$ are the matrix elements of the operator of the dipole moment vector of the system under study; α and β are the indices of Cartesian coordinates x, y, and z; $\hbar\omega$ is the energy of the laser wave photon with a frequency ω; $\hbar\omega_{mi} = \varepsilon_m - \varepsilon_i$; and ε_m is the energy spectrum of the system. Summation in Eq. (1) is performed over the intermediate stationary states $|m\rangle$ of the system with $m \neq i$. The factor N for an arbitrary system should be omitted. In the case of a rarefied gas, the system is reduced to an atom, and the factor N, appearing in front of the sum, is understood as the concentration of atoms in the gas. Expression (1) holds true also for a crystal medium if only bound electrons are taken into consideration. In the latter case, the factor N stands for the number of unit cells per unit volume.

To simplify the final formulas, we assume that the electric fields of laser waves are linearly polarized along the direction of the x-axis. Then, it is sufficient to restrict our consideration to a single tensor element $\chi_{xx}^{(1)}(\omega)$. We will denote this quantity as $\chi_{xx}^{(1)}(\omega) = \chi^{(1)}$, omitting the coordinate indices.

In what follows, Rydberg states will be denoted as $|n\rangle$. We set $|i\rangle = |n\rangle$ and represent $\chi^{(1)}$ as a sum of two terms: $\chi^{(1)} = \chi_{Ry}^{(1)} + \chi_{rest}^{(1)}$. The term $\chi_{Ry}^{(1)}$ is given by Eq. (1) with $|i\rangle = |n\rangle$, $|m\rangle = |n_1\rangle$, $n \neq n_1$. Thus, we need to perform summation in Eq. (1) only over the Rydberg states different from fixed $|n\rangle$. In contrast to the first term, the second term $\chi_{rest}^{(1)}$ involves summation over $m \neq n_1$. In other words, summation has to be made in this case over all the states except for the Rydberg ones. We will consider nonresonant cases, when $\omega \neq \omega_{ml}$ for all the discrete states m and l.

To estimate $\chi_{rest}^{(1)}$, it is sufficient to set $d_a = ea$ (a is the atomic scale on the order of the Bohr radius). This approximation holds true for, at least, several atomic transitions with maximum values of d_{ml}. Under nonresonant conditions, all the denominators of the form $\hbar\omega \pm \hbar\omega_{ml}$ can be replaced by $\hbar\omega_a$, where ω_a is some typical atomic transition frequency ($\hbar\omega_a = e^2/a = 2$Ry, where Ry is the Rydberg constant). Using these approximations, we reduce Eq. (1) to $\chi_{rest}^{(1)} = -N(d_a)^2(\hbar\omega_a)^{-1} = -Na^3$. The same result can be obtained if we estimate the susceptibility of a gas with atoms residing in the ground state, $\chi_a^{(1)} = -Na^3$, since $|i\rangle$ in Eq. (1) in this case is related to the ground state, and summation over $m = n_1$ gives a negligible contribution. Thus, we finally have $\chi_{rest}^{(1)} = \chi_a^{(1)}$. If, for example, $a \approx 10^{-8}$ cm and $N \approx 10^{19}$ cm^{-3}, then $\chi_a^{(1)} \approx 10^{-5}$.

Now, we use a similar approach to estimate $\chi_{Ry}^{(1)}$. The electron density distribution in an RA reaches its maximum at the distance on the order of $r_{Ry} \sim n^2a$. Therefore, we can employ the following order-of-magnitude estimate: $d_{nn_1} \approx n^2ea = d_{Ry}$ (e.g., $d_{nl-1,nl} = ea\frac{3}{2}n\sqrt{n^2-l^2} \approx n^2ea$ for $l \ll n$ [27]). Then, for Rydberg levels, $\varepsilon_n = -\frac{1}{2n^2}\frac{e^2}{a} = -\frac{\text{Ry}}{n^2}$, we find that $\omega_{n,n-1} = \frac{\omega_a}{n^3} \ll \omega$. Substituting $\omega_{n,n-1}$ and $d_{nn_1} \approx d_{Ry}$ for $\chi_{Ry}^{(1)}$ and d_{nn_1} in Eq. (1), we arrive at the following estimate for ω_{n_1n} linearly depending on the principal quantum number n:

$$\chi_{Ry}^{(1)} = -2N\frac{d_{Ry}^2}{\hbar\omega^2}\omega_{n,n-1} = -2n(Na^3) = 2n\chi_a^{(1)}. \quad (2)$$

Hence, we find that, with $n \gg 1$, the absolute value of $\chi_{Ry}^{(1)}$ is much greater than the linear susceptibility $\chi_a^{(1)}$ of a conventional gas and $\chi_{rest}^{(1)} = \chi_a^{(1)}$. Therefore, we can assume with a satisfactory accuracy that the linear

susceptibility of a Rydberg gas is $\chi^{(1)} = \chi_{Ry}^{(1)} + \chi_{rest}^{(1)} \approx \chi_{Ry}^{(1)}$. In other words, we can completely neglect the contribution of all the intermediate states except for the Rydberg ones.

Expanding Eq. (1) as a series in a small parameter $\omega_{n_1 n}/\omega$, we derive a more accurate expression for $\chi^{(1)}$:

$$\chi_{Ry}^{(1)} = \chi^{(1)} = -\frac{2N}{\hbar\omega^2}\sum_{n_1}|d_{nn_1}|^2\omega_{n_1 n}$$

$$-\frac{2N}{\hbar\omega^4}\sum_{n_1}|d_{nn_1}|^2(\omega_{n_1 n})^3 - \dots \qquad (3)$$

We can now use the sum rule, which is well known in atomic physics [27]: $\sum_{n_1}|d_{nn_1}|^2\omega_{n_1 n} = \dfrac{e^2\hbar}{2m}$. Invoking this rule and restricting our analysis to the first term in Eq. (3), we arrive at the following result:

$$\chi_{Ry}^{(1)} = \chi^{(1)} = -\frac{e^2 N}{m\omega^2}. \qquad (4)$$

This expression also gives the linear susceptibility of a rarefied gas of free electrons in the classical model. This is not surprising, since the coupling of an electron with an ion in an RA is weak as compared with the photon energy in the optical range. For the convenience of our further analysis, we will represent Eq. (4) in another form. We introduce the electromagnetic radius of an electron $r_e = \dfrac{e^2}{mc^2}$ and the wavelength of optical field $\Delta = \lambda/2\pi = c/\omega$ to arrive at

$$\chi_{Ry}^{(1)} = \chi^{(1)} = -(Nr_e\Delta^2). \qquad (5)$$

The identity of Eqs. (2) and (5) implies that $n = 0.5r_e\Delta^2 a^{-3}$. Substituting the values $r_e = 10^{-13}$, $a = 0.5 \times 10^{-8}$ cm, and $\Delta = 10^{-5}$ cm into this expression, we find that $n = 40$. This result clearly shows that our approximations and Eq. (2) for $\chi_{Ry}^{(1)}$ are quite adequate for reliable estimates on n within the interval of $n \sim 10$–100.

To demonstrate our method of estimation of nonlinear susceptibilities, we will consider susceptibilities $\chi_{\alpha\beta\gamma\delta}^{(3)}(\omega_1, \omega_2, \omega_3)$ responsible for nonlinear-optical effects of the third order, such as third-harmonic generation (THG), four-wave mixing, self-focusing, self-phase modulation, two-photon absorption, stimulated Raman scattering, etc. To make these estimates, we will employ the approximations substantiated above for the estimation of $\chi_{\alpha\beta}^{(1)}(\omega)$. In particular, to describe THG in linear polarized laser waves with the same polarizations, we should estimate $\chi_{xxxx}^{(3)}(\omega, \omega, \omega) = \chi^{(3)}$ (tensor indices and arguments will be omitted below for the sake of convenience). The well-known expression for $\chi^{(3)}$ is written as [28, 29]

$$\chi^{(3)} = \frac{N}{\hbar^3}\sum_{im_1m_2m_3}\rho_i^{(0)}d_{im_1}d_{m_1m_2}d_{m_2m_3}d_{m_3i}$$

$$\times \{[(3\omega - \omega_{m_1i})(2\omega - \omega_{m_2i})(\omega - \omega_{m_3i})]^{-1}$$

$$- [(\omega + \omega_{m_1i})(2\omega - \omega_{m_2i})(\omega - \omega_{m_3i})]^{-1} \qquad (6)$$

$$+ [(\omega + \omega_{m_1i})(2\omega + \omega_{m_2i})(\omega - \omega_{m_3i})]^{-1}$$

$$- [(\omega + \omega_{m_1i})(2\omega + \omega_{m_2i})(3\omega + \omega_{m_3i})]^{-1} \}.$$

This susceptibility can be also represented as a sum of two terms: $\chi^{(3)} = \chi_{Ry}^{(3)} + \chi_{rest}^{(3)}$. Each of these terms is given by Eq. (6) with different types of summation: for $\chi_{Ry}^{(3)}$, $|m_j\rangle = |n_j\rangle$, where $j = 1, 2, 3$ and n_j is the principal quantum number of Rydberg states, and for $\chi_{rest}^{(3)}$, $|m_j\rangle \neq |n_j\rangle$. Using the same assumptions as those employed above to estimate $\chi_{rest}^{(1)}$, we find that the expression for $\chi_{rest}^{(3)}$ coincides with the relevant nonlinear susceptibility $\chi_a^{(3)}$ for a rarefied gas of ground-state atoms:

$$\chi_{rest}^{(3)} = \chi_a^{(3)} = -\frac{N d_a^4}{\hbar^3\omega_a^3} = -(Na^3)\frac{a^4}{e^2} = -Na^3\frac{1}{E_a}. \qquad (7)$$

In the final formula (7), $E_a = e/a^2$ is a typical value of the intraatomic electric field. Setting $E_a = 10^7$ esu, $N = 10^{19}$ cm^{-3}, and $a = 10^{-8}$ cm, we find that $\chi_{rest}^{(3)} = \chi_a^{(3)} = \chi_a^{(1)}(E_a)^{-1} = 10^{-12}$ esu.

Finally, we can estimate $\chi_{Ry}^{(3)}$ using the same approach as that employed above to find $\chi_{Ry}^{(1)}$. Performing simple algebraic calculations involving series expansions of expressions of the form of Eq. (6) in a small parameter, we derive

$$\chi_{Ry}^{(3)} = -\frac{1}{9}\frac{N}{\hbar^3}\frac{d_{Ry}^4}{\omega^3}\frac{\omega_{n, n-1}}{\omega}$$

$$\cong -(Na^3)\frac{1}{9}n^8\frac{d_a^2}{(\hbar\omega_a)^2}\frac{1}{n^3} = -(Na^3)\frac{n^5}{9E_a}, \qquad (8)$$

where we used the notations $\omega = \omega_a$, $d_{Ry} = n^2 d_a$, and $\omega_{n, n-1} = \omega_a/n^3$ for the final formulas.

As can be seen from the final expression (8), $\chi_{Ry}^{(3)} = \chi^{(3)} = \chi_a^{(3)}\dfrac{n^5}{9}$, i.e., $\chi_{Ry}^{(3)}$ is a power function (of the fifth power). With $n = 10$, we have $\chi_{Ry}^{(3)} \approx 10^4\chi_a^{(3)} \approx 10^{-8}$ esu.

Thus, $\chi_{Ry}^{(3)}$ is much greater than $\chi_a^{(3)}$. This implies that, for example, the efficiency of third-harmonic generation in a gas of RAs with a concentration $N = 10^{14}$ cm^{-3} is nearly equivalent to the THG efficiency in a gas of ground-state atoms with the concentration $N_a = 10^{19}$ cm^{-3}.

Thus, RAs in the gas phase possess very high nonlinear-optical susceptibilities, which is confirmed by the available experimental data. However, we should expect that RAs may exist not only in the form of a gas, but, although it may seem paradoxical, in a liquid or even a solid-state phase of matter, where nonlinear susceptibilities are also very high.

3. CONDENSED PHASE OF RYDBERG ATOMS (RYDBERG MATTER)

At first glance, formation of Rydberg matter is impossible, since the lifetime of an excited atom is very short—about 10^{-8} s. Then, such an atom is transferred to the ground state emitting a photon. An excited atom may relax even faster through an Auger process when it collides other excited atoms. In this case, an electron of the first atom transfers its energy to an electron of another atom, which becomes ionized as a result of this collision, while the first atom is transferred to the ground state.

Nevertheless, condensed excited states may arise under certain conditions, and the existence of such states is currently a well-documented fact.

The idea of producing a metallized phase in a gas was put forward back in 1980 [30]. The theory of CES, based on the method of density functional [9] (see also references in [13] and review papers [10, 31]), was developed several years later.

Formation of CES and RM starts with the condensation process caused by the polarization (van der Waals) mutual attraction of Rydberg atoms toward each other. For Rydberg atoms, this attraction is n^7 times stronger than for nonexcited atoms or molecules. When the electron shells of RAs overlap, i.e., for interatomic distances comparable with RA sizes, exchange interactions come into play. These interactions determine elastic repulsive forces and the mean stable distance between RAs in metastable RM.

When the electron shells of RAs overlap, an electron may move with equal probabilities around its parent ion and around the neighboring ions before it relaxes to a lower lying state. Such valence electrons in a cluster are usually called delocalized, or collectivized

electrons. The area of motion of electrons substantially expands under these conditions. The sizes of this area increase as quantities multiple of the number of atoms in a cluster. This leads to an even sharper decrease in the kinetic energy of electrons in clusters consisting of RAs relative to an H_2 hydrogen molecule. As a consequence, the coupling energy becomes rather large: an RA cluster becomes stable with respect to evaporation of Rydberg atoms. These effects are similar to the formation of metals of alkaline and alkaline–earth atoms. In this sense, a cluster can be considered as a structure consisting of a metallized condensed phase, i.e., the phase of RM.

General description of the physical properties of RM is usually provided in terms of a simple model of an RA cluster. A cluster in this case is understood as an assembly of RAs closely packed into a face-centered cubic or closely packed hexagonal structure, characteristic of solid-state crystals or the near order in liquids. An elementary model consists of identical RAs residing in spherically symmetric S states. With large quantum numbers n, spherically symmetric S states still exist. An electron cloud with $n \gg 1$ in the S state radically changes in this case from the electron cloud with $n = 1$. In the considered case, the electron cloud is concentrated within a narrow layer with a thickness na_{Br} near the surface of a sphere with the radius n^2a_{Br}. An RA in the S state can be considered as a *hollow* atom, similar to a bubble, since the density of the electron cloud on the nucleus and in most of the inner part of the atomic volume is negligibly small. For substantially asymmetric states, toruslike RAs are usually considered. In both cases, a minimum-size cluster consists of seven RAs and has a shape of a planar hexagon. A minimum three-dimensional cluster of spherical RAs consists of 13 closely packed RAs. All the valence electrons in RM are collectivized and are concentrated in thin layers along the boundaries of centered unit cells (Wigner–Seitz cells). Clusters of larger sizes are constructed by adjoining additional atoms to minimum-size clusters. Spatially extended crystal samples with macroscopic sizes may arise in this manner.

An Ashcroft pseudopotential can be employed instead of the Coulomb potential to describe the interaction between an electron and a nucleus (or an electron and an ion core) within the framework of the considered model. The Ashcroft pseudopotential eliminates the singularity characteristic of the Coulomb potential, replacing this singularity by a step in the central area of an RA, where the nucleus with electrons of inner atomic shells is located, i.e., in the region of the ion core. In the first-order approximation, this replacement does not have a significant influence on the accuracy of calculations. The electron cloud of a valence electron has a very low density around the ion core, i.e., around the step. Parameters of this step are chosen in such a way as to give correct values of energy and the

electron density distribution in an isolated RA. The introduction of a pseudopotential and the use of the method of density functional allows a variation procedure to be employed for the determination of the minimum energy density in RM.

This theory has much in common with the general method of calculation of physical parameters for simple metals. The difference is that, in the case of simple metals, e.g., alkaline metals, the lower energy states of the ion core are filled with electrons, while the lower states in RM are vacant. However, this difference has no influence on the main physical and chemical properties of metals and RM, since these properties are determined by valence electrons. The presence or absence of electrons in lower levels (inside ion cores) influences only the lifetime of metastable RM.

The CES theory allows many parameters and properties of RM to be calculated in a rather simple way or reliably estimated for different initial principal quantum numbers n. In particular, this approach can be used to assess interatomic distances, the equilibrium density, the coupling energy, elasticity modulus, the coefficient of surface tension, the speed of sound, the melting point, the boundary of the transparency range, the Fermi level, electric conductivity, and many other parameters.

The most important achievement of the above-developed approach relative to the method employed for the calculation of metal parameters is associated with the fact that the distribution of the electron density (e-density) in RM is quite nonuniform. In simple metals, the e-density remains virtually constant within the Wigner–Seitz cell. The e-density in RM differs from zero around the boundary of the Wigner–Seitz cell. According to the results of numerical simulations, the behavior of e-density and especially the behavior of a single-electron potential (e-potential) are quite unusual. The e-potential displays a clearly pronounced minimum wherever the e-density reaches clearly pronounced maxima! This is due to the fact that the exchange interaction brings electrons to the area of increased e-density. A similar effect has been known for a long time in the theory of metals. This effect is described by the Slater exchange potential $V_{exc}(r) = -\alpha[\rho(r)]^{1/3}$, where $\rho(r)$ is the e-density at the point r and $\alpha \cong 2$ eV is a constant. The contribution of this effect in usual metals is normally several percent. In the case of RM properties, this effect plays a crucial role.

This important conclusion of CES theory is a physical manifestation of the compensation of e–e interaction due to the identity of electrons as Fermi particles whose quantum state in RM is described by an antisymmetric wave function.

More detailed calculations show that conductivity electrons are accumulated around the minima of the e-potential in the form of a degenerate electron gas, giving rise to a potential barrier for the penetration of conductivity electrons to the center of the Wigner–Seitz cell. Thus, the exchange interaction, on the one hand, assists the stabilization of the system, on the other hand, may considerably increase the lifetime of the metastable RM state up to macroscopic time intervals on the order of several minutes. The latter effect was observed experimentally.

The experimental results have been obtained using new techniques to create large densities of highly excited Rydberg species. Alkaline atom Rydberg species are generally simplest to form because of the low ionization energy of alkaline atoms. The new techniques employ diffusion of alkaline ions from the bulk of nonmetallic materials. For example, in the case of graphite surfaces, it was shown that the emission of Cs^+ ions gives rise to a nearly resonant process that forms Rydberg species from the emitted ions and thermal electrons. By increasing the pressure of Cs vapor in contact with such surfaces and by ensuring that diffusion takes place in the material, high densities of Cs and K Rydberg species have been achieved. Small particles (clusters) and macroscopic amounts of RM can be produced by using Cs vapor. Alkaline-doped metal-oxide surfaces (e.g., promoted catalyst surfaces) have been also shown to provide high densities of K Rydberg species. The behavior observed for RM produced by such methods qualitatively agrees with theoretical predictions: RM is, for example, transparent to the visible light and emits much less light than an ordinary plasma would when high currents are carried. The observed matter is very energetic, which is easy to observe through explosions of the matter under simultaneous emission of the visible light or charged particles for both small particles of RM and large layers of RM on surfaces. A more detailed discussion can be found in [10, 13].

Since the first experimental observations of RM in a cesium metal plasma, spectroscopic studies of this highly excited form of condensed matter have been performed [32]. Electronic Raman anti-Stokes and mixed Stokes processes have been detected in the range of 290–920 nm upon nonresonant excitation at 564 nm using a nanosecond pulsed dye laser. No fluorescence was observed in this first Raman study of the RM form of Cs. Stokes transitions have been mixed in one more step with laser radiation and go from low circular Cs^+ states to RM states. Thus, it was concluded that Raman spectroscopy in general should be the most useful method to study RM due to the extremely large polarizability of highly excited Rydberg states, forming the RM phase by condensation.

It was shown recently [33] that much less powerful radiation of cw IR lasers also interacts with RM through stimulated Raman processes, revealing novel features of RM and opening more possibilities for systematic studies of various density regimes of RM exist-

ence. It was found that the wave-number blue shifts of single-mode laser radiation in low-density RM are due to the stimulated Raman process. In this case, RM is mainly produced from Rydberg states of K atoms. These experiments were performed with milliwatt cw lead salt tunable diode lasers. Blue shifting was observed as shifts of Fabry–Perot etalon fringes and was on the order of 0.05 cm^{-1}. This blue shifting is attributed to a complete conversion to anti-Stokes radiation through higher order stimulated Raman shifting by extremely small quanta from the near continuum of energy levels in the metallic Rydberg matter phase. The high efficiency of the stimulated Raman process is believed to be partially due to the weak coupling with other degrees of freedom.

Recent experiments have also demonstrated stimulated anti-Stokes Raman scattering from an RM surface boundary layer on the sample of the same type as the one used in [33]. These experiments were performed with a low-intensity He–Ne laser with a spectrometer used to analyze the light coming from the sample antiparallel to the laser beam. The anti-Stokes lines from K atoms, as well as from H$_2$ and other small molecules were also observed along with RM transition bands [34]. The corresponding Stokes features were not observed, which is a direct indication of the inversion of the system, in agreement with assumptions and demonstrations of [33].

Rydberg matter, i.e., a condensed phase of excited atoms and molecules, was predicted more than 20 years ago. Comprehensive quantum-mechanical calculations have been performed to predict different properties and the lifetime of RM. These calculations have shown that RM is a long-lived excited state of matter. According to theoretical predictions, the RM lifetime may be as long as 10 min or even several hours and days. These predictions are consistent with long radiative lifetimes of even isolated circular Rydberg atoms. (The lifetime averaged over the angular momentum quantum number is 0.18 s for $n = 40$ and 17 s for $n = 100$ [32].) De-excitation was found to occur mainly due to the Auger processes [10] involving two electrons, which simultaneously change their energies and orbital momenta. It was demonstrated in [33] that RM has a rather long relaxation time for electronic excitation with a lower limit of 10 ms.

Rydberg matter may be involved in many natural phenomena both on Earth and in the interstellar space. The hypothesis that RM may be very common in interstellar space has been accentuated by studies showing a good agreement with the so-called unidentified infrared (UIR) bands, which dominate the emission spectrum from interstellar space [35]. Rydberg matter is on the borderline between the classical and quantum-mechanical descriptions of matter and is, therefore, of considerable fundamental importance. In this context, Holmlid [36] proved recently that all of the highly excited electrons have to more in one plane. Thus, RM, at least

in its highly excited states, has a form of monolayers of atoms. Because of the low surface work function of RM (according to theoretical predictions and experimental results [13], its values fall within the range of 0.2–0.8 eV), many applications become possible in the area of power electronics, energy conversion, optoelectronics, and, perhaps, quantum computing.

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