The energy spectrum and other properties of localized electron states in condensed media

E. P. Bashkin

Institute for Physical Problems, Academy of Sciences of the USSR
(Submitted 11 January 1982)
Zh. Eksp. Teor. Fiz. **82**, 1868–1885 (June 1982)

The shift and splitting of a shallow electron level, induced by extraneous magnetically polarized particles, are computed. In a magnetic field this interaction leads to a change in the magnitude of the Zeeman splitting. The helium-vapor-induced shift of the spectrum of electron states above the surface of liquid helium, a shift which explains a number of experimental data, is determined. The influence of point defects on the spectra of the shallow impurity levels and the Wannier-Mott excitons in a semiconductor is investigated. It is shown that the action of the plasma background on a radiating ion leads to appreciable shifts and the disappearance of certain spectral lines in a dense plasma. Thermodynamic instabilities, magnetic phase transitions, specific high-frequency oscillations, and the appearance of a new EPR frequency in the investigated systems are considered.

PACS numbers: 71.70.Ej, 71.50. + t, 67.20. + k, 52.25.Ps

The spectroscopy of the localized electron states in condensed media depends essentially on the properties of these media. Even a rarefied gaseous medium changes quite appreciably the energy levels of a bound electron as compared with the spectrum in a vacuum, up to the point of complete disappearance of localized discrete states. In the present paper we study the shift of a shallow electron level under the action of an external system of extraneous scattering centers. If for some reasons the medium is magnetically polarized, then the interaction of the electron with the medium lifts the spin degeneracy, and the energy level is split (even in the absence of a magnetic field!). In an external magnetic field the quantum refraction of the bound electron on the particles of the medium changes the mutual disposition of the Zeeman lines in the spectrum.

Besides the change in the depth of the level, caused by the direct interaction of the localized electron with the medium, a substantial contribution to the energy shift is made also by the screening by the medium molecules of the interaction between the electron and the center attracting it. The shift and splitting of a shallow electron level by a neutral medium are computed in the particular cases of the spectroscopy of highly excited atoms in an extraneous-gas atmosphere, electrons localized above the surface of liquid helium, and bound electron states of large radius (impurity levels, Wannier–Mott excitons) in semiconductors with point defects. Everywhere in the computations we consider only elastic scattering, i.e., we assume the velocities to be sufficiently low, so that the internal structure of the particles does not change during their collisions. We also carry out numerical estimates and a comparison with the available experimental data.

The case in which the medium, although quasineutral, consists of charged particles is considered, using as an example the interaction of a hydrogenlike ion with a surrounding plasma background in an ionized gas. The resulting effects turn out to be very significant at sufficiently high densities of the ionized gas, and should be taken into account in dense-plasma spectroscopy and diagnostics.

It is interesting that not only does the medium affect the energy spectrum of the bound electron, but the presence in the medium of a definite number of shallow discrete levels can cardinally change the macroscopic properties of the system as a whole. In the final part of the paper we consider in connection with the earlier investigated objects such phenomena, due to the presence in the medium of shallow bound states, as magnetic phase transitions, the thermodynamic instability of the gaseous phase, zero-sound vibrations and spin waves, the appearance of a second EPR frequency, and homogeneous antiferromagnetic resonance. Some of these effects can be observed by means of present-day experimental techniques.

1. LEVEL SHIFT AND SPLITTING

Let us consider a shallow localized electron state with characteristic localization extent $\bar{r}$. Let us now place such a bound electron in a rarefied medium of extraneous scattering centers with molecular density N such that

$$|\Gamma| \ll N^{-1/3} \ll \bar{r}, \tag{1.1}$$

where Γ is the amplitude of the electron scattering by a center. For definiteness, we shall now speak of a highly excited atom in a gas of neutral spin-$\frac{1}{2}$ particles. The role of the characteristic dimension $\bar{r}$ is then played by the mean distance from the excited electron to the center of the atom (it is assumed that $\bar{r}$ is considerably greater than the radius of the atomic core). As usual,[1] let us introduce the effective potential $U_{\alpha\beta,\mu\nu}(r)$ for the interaction of the electron with an extraneous-gas particle in such a way that it allows the application of perturbation theory and satisfies the renormalization condition:

$$\int U_{\alpha\beta,\mu\nu}(r)\,dV = -\frac{2\pi\hbar^2}{m}\Gamma_{\alpha\beta,\mu\nu}(0), \tag{1.2}$$

where m is the electron mass, α, β and μ, ν are the spin indices for the electron and the extraneous particle, and $\Gamma_{\alpha\beta,\mu\nu}(0)$ is the forward-scattering ampli-

0038-5646/82/061076-10$04.00

tude. Although we shall neglect the relativistic corrections stemming from the spin-orbit and spin-spin interactions, because of the exchange effects, the pseudopotential $U_{\alpha\beta,\mu\nu}$ (like the scattering amplitude $\Gamma_{\alpha\beta,\mu\nu}$) depends on the spins of the colliding particles, more exactly, on their total spin.

We shall be interested not only in the shift due to the quantum refraction of the electron by the atoms of the extraneous gas, but also in the level splitting (i.e., in the lifting of the spin degeneracy), produced by the same causes when the spin system of the scattering centers is magnetically polarized for some reason (an external magnetic field, a ferromagnetic phase transition, the injection of a polarized beam, optical pumping, etc.). Accordingly, we shall describe the gas of extraneous atoms by a polarization density matrix $n_{\alpha\beta}(\mathrm{p})$ that is a linear function of the Pauli matrices $\sigma_{\alpha\beta}$:

$$n_{\alpha\beta}(\mathbf{p})={}^1/_2(n^+ + n^-)\delta_{\alpha\beta}+{}^1/_2(n^+ - n^-)\boldsymbol{\sigma}_{\alpha\beta}\mathfrak{M}, \tag{1.3}$$

where $\mathfrak{M}$ is the unit vector in the direction of the macroscopic magnetic moment of the gas; n^+ and n^- are the Fermi occupation numbers for the extraneous particles with spins oriented along and oppositely to the direction of the magnetic polarization $\mathfrak{M}$:

$$n^{\pm}(\mathbf{p})={}^1/_2\{1-\mathrm{th}[(\varepsilon-\mu_{\pm})/2T]\}, \quad \varepsilon=p^2/2M. \tag{1.4}$$

Here T is the temperature, M is the mass of a gas particle, and the quantities $\mu_{\pm}$ are given by the normalization conditions:

$$\int n^{\pm}(\mathbf{p})\frac{d\mathbf{p}}{(2\pi\hbar)^3}=N_{\pm}, \tag{1.5}$$

where N_+ and N_- are the concentrations of the gas atoms with spins oriented parallel and antiparallel to $\mathfrak{M}$. The values of N_+ and N_- give the degree α of polarization of the gas:

$$N_+ - N_- = \alpha N, \quad N_+ + N_- = N. \tag{1.6}$$

The electron-scattering center interaction Hamiltonian has the form

$$\hat{H}=\int\hat{\Psi}_\beta^+(t,\mathbf{r})\hat{\Phi}_\nu^+(t,\mathbf{r}')U_{\alpha\beta,\mu\nu}(\mathbf{r}-\mathbf{r}')\hat{\Phi}_\mu(t,\mathbf{r}')\hat{\Psi}_\alpha(t,\mathbf{r})\,d\mathbf{r}\,d\mathbf{r}', \tag{1.7}$$

where $\hat{\Psi}_\beta^+$, $\hat{\Psi}_\alpha$ are the Heisenberg Ψ operators for the electron, $\hat{\Phi}_\nu^+$, $\hat{\Phi}_\mu$ are the corresponding operators for the atoms of the extraneous gas, and summation is implied over repeated indices. On account of (1.1) the de Broglie wavelength of the electron is much greater than the electron–extraneous particle interaction range, i.e., there occurs low-energy scattering. Therefore, in the leading—in $|\Gamma|/\bar{r}\ll 1$—approximation the scattering amplitude is a real quantity, an energy-independent constant, i.e.,

$$\Gamma_{\alpha\beta,\mu\nu}(0)=-a_{\alpha\beta,\mu\nu}.$$

The contribution made by the interaction (1.7) to the electron Green function is then determined by only one loop diagram (Fig. 1). The wavy lines in the figure correspond to the electron Green functions, and the continuous loop pertains to the atoms of the extraneous gas. Using the relation (1.2), we obtain for the self-energy function $\Sigma_{\alpha\beta}$ the expression

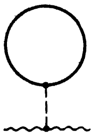

FIG. 1.

$$\Sigma_{\alpha\beta}=(2\pi\hbar^2/m)a_{\alpha\beta,\mu\nu}N_{\nu\mu}, \quad N_{\alpha\beta}=\langle\hat{\Phi}_\alpha^+\hat{\Phi}_\beta\rangle={}^1/_2N(\delta_{\alpha\beta}+\alpha\boldsymbol{\sigma}_{\alpha\beta}\mathfrak{M}). \tag{1.8}$$

The s-scattering length $a_{\alpha\beta,\mu\nu}$ can be expressed in terms of the singlet and triplet scattering lengths, $a_{\uparrow\downarrow}$ and $a_{\uparrow\uparrow}$, respectively, in the usual fashion:

$$\begin{gathered} a_{\alpha\beta,\mu\nu}={}^1/_4a_1\delta_{\alpha\beta}\delta_{\mu\nu}+{}^1/_4a_2\boldsymbol{\sigma}_{\alpha\beta}\boldsymbol{\sigma}_{\mu\nu}, \\ a_1=3a_{\uparrow\uparrow}+a_{\uparrow\downarrow}, \quad a_2=a_{\uparrow\uparrow}-a_{\uparrow\downarrow}. \end{gathered} \tag{1.9}$$

Performing the summation over the spins in (1.8), we finally find that

$$\Sigma_{\alpha\beta}=(\pi\hbar^2/2m)N(a_1\delta_{\alpha\beta}+\alpha a_2\boldsymbol{\sigma}_{\alpha\beta}\mathfrak{M}). \tag{1.10}$$

The first term in (1.10), which describes the shift of the upper atomic level in the extraneous gas, was derived by Fermi[2] (see also Firsov's paper[3]). More general expressions for the spectral-line shift, which take account of the contribution from the scattering involving nonzero spins, were found by Alekseev and Sobel'man.[4] The second term in (1.10) corresponds to the shifted-electron-level splitting, which occurs as a result of the exchange interaction during the coherent refraction of the electron by the atoms of the extraneous spin-polarized gas.

The correction (1.10) to the energy does not, however, account for the whole change in the depth of the shallow level in an excited atom placed in an extraneous gas, since the presence of the gas also changes the basic Hamiltonian corresponding to the interaction of the atomic core with the electron. Indeed, since the sphere of radius $\bar{r}$ has macroscopic dimensions, and contains a large number of atoms of the extraneous gas, the atomic core's electric field acting on the electron under consideration differs from its value in the absence of the extraneous gas by the factor $1/\varepsilon$, where ε is the permittivity, which can be determined from the Clausius–Mossotti formula:

$$(\varepsilon-1)/(\varepsilon+1)={}^4/_3\pi N\varkappa, \tag{1.11}$$

where $\varkappa$ is the polarizability of the gas.

Since we are dealing with a highly excited state of the atom, when the electron is on the average located at large distances from the atomic core, we can classify the energy levels of the electron in the atomic core's field (which at distances of the order of $\bar{r}$ can, with a high degree of accuracy, be consider to be a Coulomb field) with the aid of the hydrogenic spectrum with the Rydberg correction Δ_l (Ref. 1):

$$\mathscr{E}=-\mathscr{E}_{0n}/\varepsilon^2, \quad \mathscr{E}_{0n}=me^4/2\hbar^2(n+\Delta_l)^2, \tag{1.12}$$

where n is the principal quantum number and e is the electron charge. The correction Δ_l does not depend on N, since it is determined by the deviation of the field from the Coulomb field at distances small compared to $\bar{r}$ and $N^{-1/3}$, where the extraneous gas has no screening effect. In the approximation linear in N, we find from (1.11) and (1.12) that

$$\Delta\mathscr{E}=8\pi N\varkappa\mathscr{E}_{0n}=2(\varepsilon-1)\mathscr{E}_{0n}. \tag{1.13}$$

Besides the contributions (1.10) and (1.13) from the scattering by the electrons and the dielectric screening, the interaction of the particles of the extraneous gas with the atomic core also has an effect on the position of the level. The corresponding shift due to the polarization of the extraneous particles in the field of the atomic core turns out in the quasistatic approximation, in which

$$\chi\equiv\varkappa Ne^2/\hbar v\gg 1$$

(v is the extraneous-gas-particle velocity) to be proportional to $N^{4/3}$ (Refs. 2–4), and we shall neglect it in the linear approximation. Let us note that, in the case of elastic scattering of ultraslow foreign particles, i.e., for

$$v\ll\hbar/M^*b\sim(e^2/\hbar)(m/M^*)$$

(b is the atomic dimension and M^* is the reduced mass of the atomic core and a foreign particle), we can use for the level shift the formula (1.10) with the appropriate s-scattering-length value and the additional small factor $m/M^*\ll 1$. In the impact approximation, in which $\chi\ll 1$, the polarization-induced shift is linear[4] in N:

$$\Delta\mathscr{E}_p=\frac{3^{1/2}}{2}\cdot 11.4\left(\frac{\varkappa e^2}{2\hbar}\right)^{2/3}v^{1/3}N. \tag{1.14}$$

Thus, at sufficiently low temperatures and not too low foreign-gas densities the unperturbed shallow level $\mathscr{E}=-\mathscr{E}_{0n}$ shifts, and splits up—in proportion to the spin polarization of the foreign particles—into two levels with energies given by the formulas (1.10) and (1.13):

$$\mathscr{E}=-\mathscr{E}_{0n}+2(\varepsilon-1)\mathscr{E}_{0n}+(\pi\hbar^2/2m)N(a_1\pm\alpha a_2). \tag{1.15}$$

The expression (1.15) is the first term in the expansion of the level energy in powers of the density of the polarized foreign gas. The contribution (1.13) of the screening turns out to be of the order of the magnitude of the shift (1.10) when $n\sim 10$, but decreases with increasing n. Under experimental conditions,[5,6] the contribution (1.13) to the level shift constitutes about 10% of (1.10) when $n=30$. At higher temperatures, the linear—in N—polarization-induced shift (1.14) should be added to the level energy (1.15).

Let us discuss in greater detail the magnitude of the level splitting in a spin-polarized gas. Since the time τ_s required for the establishment of the spin equilibrium is determined by the weak relativistic interactions, $\tau_s\gg\tau$, where τ is the time required for the establishment of the momentum equilibrium. Therefore, if a beam of spin-polarized atoms is injected into an unpolarized medium, the beam particles will become Maxwellian over a time period $\tau_s\gg t\gg\tau$, but will retain their total magnetic moment, and we shall have at our disposal a magnetically polarized quasiequilibrium gas. The characteristic times τ_s are usually quite long, and are sufficient for experiments to be carried out. The magnetic polarization of the gas of foreign atoms can be achieved by means of other dynamical methods. The magnitude of the level splitting is proportional to the degree α of polarization, i.e.,

$$\Delta\mathscr{E}=(\pi\hbar^2/m)N|a_2|\alpha, \tag{1.16}$$

and is of the order of the level shift in a completely polarized gas, i.e., when $\alpha\sim 1$. The study of the time dependence of the splitting $\Delta\mathscr{E}$ at $t\gtrsim\tau_s$ will enable us to investigate the dynamics of the magnetization relaxation in a polarized gas.

If the spin polarization in the foreign gas is achieved simply by switching on an external magnetic field $\mathbf{H}$, then to the level energy must be added the Zeeman term

$$\delta\Sigma_{\alpha\beta}=-\beta\boldsymbol{\sigma}_{\alpha\beta}\mathbf{H}, \tag{1.17}$$

where β is the magnetic moment of the electron (we assume for simplicity that the atomic core does not possess a magnetic moment). Then there appear in the formula (1.15) for the split level the corrections $\pm\beta H$, respectively, and $\alpha=\tanh(\beta H/T)$. In a real experimental situation $\beta H\ll T$. Making allowance for this, we obtain for the magnitude of the level splitting in a magnetic field the formula

$$\Delta\mathscr{E}=2\beta H(1-\pi\hbar^2Na_2/2mT). \tag{1.18}$$

Thus, the exchange interaction of the valence electron with the atoms of the foreign gas in a constant magnetic field leads, depending on the sign of the exchange scattering amplitude a_2, to an increase or decrease in the distance between the components of the Zeeman doublet. Under the conditions of Mazing and Serapinas's experiment[6] on the investigation of absorption lines for the purpose of exciting the high-lying ($n=15$–50) states of Cs atoms in a Cs atmosphere and K atoms in a K vapor, for

$$N=(1.2-4.8)\cdot 10^{17}\,\mathrm{cm}^{-3},\ T=(360-520)^\circ\,\mathrm{C}$$

the relative increase in the Zeeman splitting will, in order of magnitude, be 0.1% [for Cs we have the values $a_{\uparrow\downarrow}=-4.04a_B$, $a_{\uparrow\uparrow}=-25.3a_B$, while for K we have $a_{\uparrow\uparrow}=-15a_B$, $a_{\uparrow\downarrow}=0.45a_B$ (Ref. 7), where a_B is the Bohr radius]. For $H\sim 100$ kOe this increase $\Delta\mathscr{E}-2\beta H\sim 0.1$ cm, which lies at the limits of experimental error. Higher foreign-gas densities are apparently required for a reliable detection of the effect.

2. ELECTRON STATES ABOVE THE SURFACE OF LIQUID HELIUM

As is well known, a one-dimensional localized electron state with a small binding energy is formed near the surface of liquid He and other dielectrics with a small $\varepsilon-1$ value.[8] Let us use the results obtained in the preceding section to investigate the effect of the atoms of the He vapor on the localized-electron spectrum. If the vapor density N is sufficiently high, so that the mean distance of the electron from the helium surface is significantly greater than $N^{-1/3}$, then the potential for the interaction of the electron with the interface between the two different dielectric phases of He is determined by the electrostatic-image forces, and is equal to[9]

$$U(z)=\frac{1}{4\varepsilon_G}\frac{e^2}{z}\frac{\varepsilon_G-\varepsilon_L}{\varepsilon_G+\varepsilon_L}\approx-\frac{e^2}{4z}\frac{\varepsilon_L-1}{\varepsilon_L+1}\left[1-4\pi N\varkappa\left(1+\frac{2\varepsilon_L}{\varepsilon_L^2-1}\right)\right], \qquad (2.1)$$

where ε_L is the permittivity of the liquid phase, $\varepsilon_G \approx 1+4\pi N\varkappa$ is the permittivity of gaseous He, and the z axis is oriented along the normal to the surface. The eigenvalues of the Schrödinger equation with the potential (2.1) and the energy correction (1.10) due to the effects of the quantum refraction of the electrons by the vapor atoms determine the electron-energy spectrum near the liquid-helium surface:

$$E=-\frac{Q^2me^4}{2\hbar^2n^2}\left[1-8\pi N\varkappa\left(1+\frac{2\varepsilon_L}{\varepsilon_L^2-1}\right)\right]+\frac{2\pi a\hbar^2}{m}N+\frac{p_\perp^2}{2m},$$
$$Q=(\varepsilon_L-1)/4(\varepsilon_L+1),\quad n=1,2,3,\ldots, \qquad (2.2)$$

where $a=a_1/4=0.62$ Å (Refs. 7, 8, and 10) is the electron-helium atom s-scattering length and $p_\perp$ is the electron momentum in the plane parallel to the surface. The mean distances from the surface of the electron in the states with $n=1$, 2, and 3 are respectively equal to[8] $\langle z\rangle_1=144$ Å, $\langle z\rangle_2=456$ Å, and $\langle z\rangle_3=1026$ Å. Therefore, at relatively high temperatures T (>1.5 Å for ^{4}He), when the vapor density is quite high, i.e., when $N \gtrsim 10^{20}$ cm^{-3}, we find that even in the ground state $\langle z\rangle_1 \gg N^{-1/3}$, and all the electron levels are described by the formula (2.2) with a high degree of accuracy (the higher the value of n, the better the description). The change, due to the presence of the vapor atoms, in the transition frequencies between states with different n is determined in this case only by the n-dependent term in (2.2):

$$\nu_{n_1,n_2}=\frac{n_2^2-n_1^2}{n_1^2n_2^2}\nu_0\left[1-8\pi N\varkappa\left(1+\frac{2\varepsilon_L}{\varepsilon_L^2-1}\right)\right],$$
$$\nu_0=\frac{Q^2me^4}{4\pi\hbar^3}. \qquad (2.3)$$

For $N=10^{21}$ cm^{-3} ($T\approx 3.3$ K) we have $\nu_{1,2}\approx 108$ GHz, which differs from the $\nu_{1,2}$ value at low vapor densities (see below) by 14.2%. Thus, a significant decrease in the photoresonance transition frequencies should occur at sufficiently high temperatures and vapor densities.

On the other hand, the condition $\langle z\rangle_n \gg N^{-1/3}$ is by no means fulfilled for each electron state at low temperatures and sufficiently low N values. In the states for which $\langle z\rangle_n \ll N^{-1/3}$ the presence of the helium vapor has absolute no effect, and the localized-electron spectrum is given by the expression (2.2) with $N=0$:

$$E=-Qme^4/2\hbar^2n^2+p_\perp^2/2m. \qquad (2.4)$$

Naturally, in the case in which the electrons move in directions parallel to the liquid surface, the collisions with the vapor atoms are, as before, important: it is precisely these collisions that determine, together with the scattering by the ripplons, the resonance-transition line width, which we shall not compute in the present paper. But since the thermal electron velocity $v_{Te}=(T/m)^{1/2}$, which characterizes the two-dimensional motion, is significantly lower than the characteristic velocity $v_0=Qe^2/\hbar$ ($v_{Te}/v_0\sim 0.1$ at $T\sim 1$ K) of the electron in the potential well, in the leading approximation in $v_{Te}/v_0 \ll 1$ the shift of the transition frequency between the states $|n_2\rangle$ and $\langle n_1|$ in which $\langle z\rangle_{n_2} \gg N^{-1/3}$ but $\langle z\rangle_{n_1} \ll N^{-1/3}$ is given by the difference between the energies (2.2) and (2.4):

$$\nu_{n_1,n_2}=\frac{n_2^2-n_1^2}{n_1^2n_2^2}\nu_0+\frac{\nu_0}{n_2^2}8\pi N\varkappa\left(1+\frac{2\varepsilon_L}{\varepsilon_L^2-1}\right)+\frac{\hbar a}{m}N. \qquad (2.5)$$

In the presence of gaseous helium with low density N the dominant contribution to the frequency increase (2.5) is made by the interaction of the electron with the vapor atoms. For $N=10^{18}$ cm^{-3} we find from (2.5) the values

$$\nu_{1,2}=126.9\,\text{GHz},\ \nu_{1,3}=148.9\,\text{GHz},$$

which agree well with the direct measurements reported by Grimes *et al.*[11]:

$$\nu_{1,2}=125.9\pm0.2\,\text{GHz},\ \nu_{1,3}=148.6\pm0.3\,\text{GHz}.$$

The interaction with the vapor atoms can thus explain within a definite density (N) range the fact that the observed values of the transition frequencies $\nu_{1,n}$ always turn out to be greater than the computed values in the case when the helium vapor is neglected.[8] The same systematic discrepancy has been observed for electrons localized above the surface of liquid ^{3}He.[12]

3. SHALLOW IMPURITY LEVELS AND EXCITONS OF LARGE RADIUS IN SEMICONDUCTORS WITH POINT DEFECTS

Entirely similar phenomena may prove to be important for bound electron states in crystals in the presence in them of point defects. If the defect dimension and concentration satisfy the condition (1.1), then the defects will play the role of refraction centers for the slow electron, and will cause the energy of the corresponding bound state to shift in proportion to their concentration. If the defect possesses an electron spin, and the defect system is, for some reasons or other, ferromagnetically ordered (see, for example, Ref. 13 and Sec. 6 of this paper), then besides the shift in proportion to the exchange interaction there will occur a splitting of the level. As obtains in semimagnetic semiconductors, deep impurity levels or impurity atoms with uncompensated electron spin in the inner shells can play the role of magnetic defects.

The presence of defects changes also the permittivity ε of the crystal and, consequently, the electric field acting on the electron. For a crystal with cubic symmetry, the problem of determining the bound-state spectrum of the electron in the effective-mass approximation formally coincides with the problem of finding the energy levels of the hydrogen atom. Therefore, arguing as above, we immediately obtain the shallow-impurity-level spectrum

$$E_{\alpha\beta}^{(i)}=\left[-\frac{m_ee^4}{2\hbar^2n^2\varepsilon^2}\left(1-2\frac{N_d}{\varepsilon}\frac{\partial\varepsilon}{\partial N_d}\right)+\frac{\pi\hbar^2a_1}{2m_e}N_d\right]\delta_{\alpha\beta}$$
$$+\frac{\pi\hbar^2a_2}{2m_e}N_d\alpha_d\sigma_{\alpha\beta}\mathfrak{M}_d \qquad (3.1)$$

and the Wannier–Mott exciton energy levels

$$E_{\alpha\beta,\mu\nu}^{(ex)}=\left[E^{(0)}+\frac{\hbar^2k^2}{2(m_e+m_h)}-\frac{\mu^*e^4}{2\varepsilon^2\hbar^2n^2}\left(1-2\frac{N_d}{\varepsilon}\frac{\partial\varepsilon}{\partial N_d}\right)\right]\delta_{\alpha\beta}\delta_{\mu\nu}+\frac{\pi\hbar^2}{2}N_d$$
$$\times\left(\frac{a_{1e}}{m_e}\delta_{\alpha\beta}+\delta_{\mu\nu}\frac{a_{1h}}{m_h}\right)+\frac{\pi\hbar^2}{2}N_d\alpha_d\left(\frac{a_{2e}}{m_e}\sigma_{\alpha\beta}+\frac{a_{2h}}{m_h}\sigma_{\mu\nu}\right)\mathfrak{M}_d, \qquad (3.2)$$

where m_e and m_h are the effective electron and hole masses; N_d is the number of defects in a unit volume; α_d and $\mathfrak{M}_d$ are the degree of polarization and the unit vector in the direction of the magnetic moment of the defects; $\mu^* = m_e m_h \cdot (m_e + m_h)^{-1}$ is the reduced mass; $E^{(0)}$ is the width of the energy gap in the crystal; $\hbar\mathbf{k}$ is the quasimomentum of the exciton "as a whole"; a_{1e}, a_{1h}, a_{2e}, and a_{2h} are the averaged—similarly to (1.9)—lengths characterizing the *s* scattering of the electron and hole on a defect; α, β and μ, ν are the spin indices for the electron and hole.

As can be seen from (3.1) and (3.2), in the presence of a magnetically ordered system of point defects, the impurity and exciton levels split up respectively into two and four components. The formulas (3.1) and (3.2) are valid for the states in which $\bar{r} \gg N_d^{-1/3}$ i.e., when

$$n^2 \gg \mu^* e^2 N_d^{-1/3} / \hbar^2 \varepsilon^2.$$

For crystals with $\varepsilon \sim 10$, $\mu^* \sim 0.1\, m$, and $N_d \sim 10^{18}$ cm^{-3}, this condition is fulfilled even in the $(n=1)$ ground state. The energy levels of the states in which $\bar{r} \ll N_d^{-1/3}$ and the presence of the defects is not felt in any way are given by the usual expressions [the formulas (3.1) and (3.2) with $N_d = 0$]. The experimental investigation of the transitions from such levels to levels with sufficiently large n, where $\bar{r} \gg N_d^{-1/3}$, will enable us to determine a very important characteristic of the system: the electron–defect scattering amplitude. The detection of the splitting of the appropriate spectral line will enable us to identify the phase transition into the magnetically ordered state in the system of magnetic impurities.

4. THE SHIFT AND DISAPPEARANCE OF SPECTRAL LINES IN A DENSE IONIZED GAS

Let us now consider the situation in which an assemblage of charged, and not neutral, particles plays the role of the medium in which the bound electron is located. Specifically, we shall consider the effect of a surrounding plasma background on the spectrum of a hydrogenlike ion (or a hydrogen atom). The dominant contribution to the level shift will then be made by the screening of the field of the nucleus of the ion by the electrons and ions of the surrounding plasma as a result of the long-range character of the Coulomb interaction. If the radius $\bar{r}$ of the electron orbit of the unperturbed hydrogenlike ion is smaller than the mean distance $N_{e0}^{-1/3}$ between the electrons of the plasma background, i.e., if

$$a_B N_{e0}^{1/3} \ll 2Z / [3n^2 - l(l+1)], \tag{4.1}$$

where Z is the charge of the ion's nucleus and n and l are the principal and orbital quantum numbers, then there will be no collective screening of the nuclear charge by the self-consistent field of the plasma, since at such distances the continuous-medium approximation for the plasma in unsuitable and the macroscopic equations for the self-consistent field are inapplicable. In this situation only a microscopic treatment of the interaction of the individual electrons and ions with the nucleus and the localized electron makes sense. The energy levels and the wave functions of the states for which the condition (4.1) is fulfilled are consequently given by the "unperturbed" expressions

$$E_n^{(0)} = -Z^2\,\mathrm{Ry}/n^2, \quad \mathrm{Ry} \equiv me^4/2\hbar^2, \quad \psi_{nlm}^{(0)} = R_{nl}(r)\, Y_{lm}(\theta, \varphi),$$
$$R_{nl}(r) = -\frac{2^{l+1}}{n^2} \frac{[(n-l-1)!]^{1/2}}{[(n+l)!]^{3/2}} e^{-Zr/a_B} \left(\frac{Zr}{a_B}\right)^l L_{n+1}^{2l+1}\left(\frac{2Zr}{a_B}\right), \tag{4.2}$$

where the $Y_{lm}(\theta, \varphi)$ are the spherical functions and the $L_q^p(x)$ are the generalized Leguerre polynomials.

On the other hand, for the states in which $\bar{r} \gg N_{e0}^{-1/3}$, the screening effect of the plasma background is very important. Indeed, in this case the averaging of the microscopic fields over small volumes (each of which, however, contains a large number of particles) reveals the existence in the plasma of a macroscopic electric field, which changes to a large extent the force field acting on the bound electron. In contrast to the localized-electron state, which is described by a wave function, the state of the medium is specified by assigning macroscopic variables: the electron density N_e and the number N_a of ions of the kind a in a unit volume. Let us place the ion in question at the coordinate origin. The presence of the plasma background modifies the electric field of the nucleus at distances $r \gg N_e^{-1/3}$ in accordance with the Poisson equation:

$$\Delta\Phi = -4\pi e \left(\sum_a Z_a N_a - N_e\right),$$
$$\Phi(r \to 0) = Ze/r, \quad \Phi(\infty) = 0, \tag{4.3}$$

where Z_a is the charge of the ion of the kind a. The bound electron state in the distorted potential $e\Phi$ of the nucleus is given by the solution to the Schrödinger equation

$$\Delta\psi + \frac{2m}{\hbar^2}(E + e\Phi)\psi = 0. \tag{4.4}$$

The localized electron cloud also produces a macroscopic electric field φ:

$$\Delta\varphi = 4\pi e |\psi|^2, \tag{4.5}$$

where $\varphi(0)$ is finite, while $\varphi(\infty) = 0$. To obtain a closed system of equations for the self-consistent field, we must further add the relations expressing the concentration distribution for the particles of the plasma background in the electric field of the nucleus and the bound electron:

$$N_e = N_{e0} \exp[e(\varphi + \Phi)/T_e], \quad N_a = N_{a0} \exp[-Z_a e(\varphi + \Phi)/T_i]. \tag{4.6}$$

Here N_{e0} and N_{a0} are the density values obtaining at points infinitely far away from the ion in question, and satisfying the electrical-neutrality condition

$$N_{e0} = \sum_a Z_a N_{a0},$$

while T_e and T_i are the electron and ion temperatures.

Equations similar to (4.3)–(4.6) have been used by Skupsky[14] to numerically compute the shift of the neon Lyman-α line for $N_{e0} \sim 10^{24}$ cm^{-3}. Let us emphasize that the results obtained by Skupsky[14] are in fact only qualitative, since the states considered by him do not fulfill the condition $\bar{r} \gg N_{e0}^{-1/3}$, and Eqs. (4.3) and (4.6) are valid only when this condition is fulfilled. We shall investigate the analytic solutions to (4.3)–(4.6), using natural simplifying circumstances.

Owing to the slight nonideality, i.e., because $e^2N_{e0}^{1/3}/T \ll 1$, we can always linearize the equations (4.6). The numerical solution, undertaken by Skupsky,[14] of the exact equations (4.3)–(4.6) goes beyond the required accuracy, since, as shown by Gurevich (see, for example, Ref. 15), the expansions of N_e and N_a may contain terms, proportional to $(\varphi+\Phi)^{3/2}$, that are not contained in (4.6). Linearizing the expressions (4.6) for N_e and N_a, substituting the resulting expressions into Eq. (4.3), and using the electrical-neutrality condition, we obtain the equation

$$\Delta\Phi-\beta^2\Phi=\beta^2\varphi, \tag{4.7}$$

where we have introduced the Debye screening distance r_D:

$$r_D^{-2}=\beta^2=4\pi e^2\left(N_{e0}/T_e+\sum_a N_{a0}Z_a^2/T_i\right). \tag{4.8}$$

If the unperturbed bound-electron state (4.2) is such that $N_{a0}^{-1/3} \ll \bar{r} \ll r_D$, i.e., if

$$\frac{1}{a_B N_{a0}^{1/3}} \ll \frac{3n^2-l(l+1)}{2Z} \ll \frac{r_D}{a_B}, \tag{4.9}$$

then the level shift due to the electrostatic screening can be computed in the form of a perturbation theory series in powers of $\bar{r}/r_D \ll 1$.

Let us make the assumption (to be confirmed by the results) that in first order perturbation theory the wave function of the localized electron state does not change under the action of the plasma background. In this case the potential φ of the electric field produced by the bound electron also does not change, and coincides with the unperturbed solution to Eq. (4.5), a solution which we shall denote by $\varphi^{(0)}$ [$\varphi^{(0)}$ is the solution to Eq. (4.5) with $\psi=\psi^{(0)}$]. The solution to the inhomogeneous equation (4.7) is given by the convolution of the Green function

$$G(\mathbf{r},\mathbf{r}')=-\frac{1}{4\pi}\frac{\exp(-\beta|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}$$

of the homogeneous equation with the right member of (4.7):

$$\Phi(\mathbf{r})=Ze\frac{\exp(-\beta r)}{r}-\frac{\beta^2}{4\pi}\int\frac{\exp(-\beta|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}\varphi^{(0)}(\mathbf{r}')d\mathbf{r}'. \tag{4.10}$$

The correction due to the contribution of the localized electron then turns out to be of second order in smallness in $\beta\bar{r} \ll 1$, and we finally obtain in the first approximation the natural result

$$\Phi(\mathbf{r})=Ze/r-Ze/r_D. \tag{4.11}$$

Since the perturbation due to the plasma screening turns out to be a r-independent constant, all the off-diagonal matrix elements are equal to zero, and, as was assumed, the ψ function of the electron remains unchanged up to the second-order terms. The level shift is linear in β, and does not depend on the quantum numbers:

$$\Delta E=Ze^2/r_D, \tag{4.12}$$

i.e., the energy levels of all the states for which the condition (4.9) is fulfilled shift by the same amount determined by the formula (4.12). The frequencies of the radiative transitions between these states clearly do not change in this approximation. On the other hand, the frequencies of the transitions between the states (4.9) and the states (4.1), in which the presence of the plasma background can be ignored, undergo, according to (4.12), a shift toward the blue region of the spectrum:

$$\frac{\Delta\nu_{n_1,n_2}}{\nu^{(0)}_{n_1,n_2}}=\frac{2}{Z}\frac{n_1^2n_2^2}{n_2^2-n_1^2}\frac{a_B}{r_D}, \tag{4.13}$$

where $\nu^{(0)}_{n_1,n_2}=(E^{(0)}_{n_2}-E^{(0)}_{n_1})/2\pi\hbar$ is the unperturbed transition frequency.

At high electron and ion densities, such as obtain in a laser plasma, the shift (4.13) can be quite substantial, and allowance for such a shift is important for the spectroscopy and diagnostics of a dense plasma. In a superdense plasma (i.e., a plasma for which $1 \lesssim N_{e0}^{1/3}a_B < Z$) with a sufficiently high degree of nonideality

$$\bar{r}/r_D \sim (e^2N_{e0}^{1/3}/T)^{1/2}$$

the blue shift (4.13) of the spectral line for the transitions into the ground state, $\Delta\nu_{1,n}/\nu^{(0)}_{1,n}$, can attain a value of the order of 1–10%. We can, by making simple estimates, easily verify that at sufficiently high values of Z, N_{e0}, and N_{a0} the shift (4.13) is significantly greater than the line width.

If the charge of the ion in question is sufficiently high, the perturbing action of the bound electron on the charged particles of the plasma background in the Debye sphere can be neglected. In this case the dominant contribution to the self-consistent field is made by the free plasma electrons and ions ($N_{e0} \gg 1, N_{a0} \gg 1$), which distort the potential of the nucleus of the ion under consideration. The spectrum of the localized electron states is then determined by the eigenvalues of the Schrödinger equation (4.4) with the screened Coulomb potential

$$U(r)=-e\Phi(r)=-Ze^2e^{-\beta r}/r. \tag{4.14}$$

We shall determine the depth of the ground s level with the aid of the variational method with the trial wave function[16]

$$\psi(r)=(2/\pi)^{1/2}\tilde{\alpha}^{3/2}\exp(-\tilde{\alpha}r), \tag{4.15}$$

where $\tilde{\alpha}$ is the Ritz variational parameter. Minimizing the total energy

$$\int\psi^*\left(-\frac{\hbar^2}{2m}\Delta+U\right)\psi d\mathbf{r},$$

we easily find the ground-state energy E_1:

$$E_1=-\frac{Ze^2}{r_D}\frac{q^3(q-1)}{4(q+1)^3},\quad Z\frac{r_D}{a_B}=\frac{(1+q)^3}{2q(q+3)}. \tag{4.16}$$

The formula (4.16) determines the dependence of the ionization potential of the ground state on the temperature and density of the plasma background. When $r_D \gg a_B/Z$ the expression (4.16) goes over, as it should, into the unperturbed formula (4.2) with the correction (4.12), i.e.,

$$E_1=-Z^2\,\mathrm{Ry}+Ze^2\beta.$$

For $r_D \lesssim a_B/Z$ the potential (4.14) does not admit of a single bound state.

Thus, the ion energy levels with the lowest principal-quantum-number values

$$n \ll (Z/a_B N_{e0}^{1/3})^{1/2} \equiv n_1$$

can be classified with the aid of the normal hydrogenic spectrum (4.2). For higher n values, i.e., those such that

$$n_1 \ll n \ll n_0, \quad n_0 = (Z r_D / a_B)^{1/2},$$

the depth of each level decreases in accordance with the expression (4.12), and, consequently, the Debye screening leads in the case of the transitions between such states and the states with small $n (\ll n_1)$ to blue spectral-line shifts proportional to $r_D^{-1} \propto (N_{e0}/T)^{1/2}$. Finally, for the high quantum-number values, i.e., for $n \sim n_0$, the classification of the levels of the one-electron ion in question differs very greatly from the hydrogenic classification. If n_0 is sufficiently high, then the spectrum of the states with $n \gtrsim n_0$ can be determined with a high degree of accuracy from the quasiclassical quantization conditions:

$$(2m)^{1/2} \oint (E - U_l)^{1/2} dr = 2\pi\hbar (n - l - 1/2), \quad U_l = U(r) + \hbar^2 l(l+1)/2mr^2. \tag{4.17}$$

The energies of the high-lying s levels, for example, are given by the following equations:

$$\int_0^\infty \frac{y^{1/2}}{y+1} \frac{z}{z+1} dy = \frac{2\pi}{\varkappa_E r_D}\left(n - \frac{1}{2}\right) \qquad \varkappa_E = \frac{(2m|E|)^{1/2}}{\hbar};$$
$$\gamma_E \frac{e^{-z}}{z} - 1 = y, \quad \gamma_E = \frac{Ze^2}{|E| r_D}. \tag{4.18}$$

In contrast to the hydrogenic spectrum, the potential field $U(r)$, (4.14), has, in any case, a finite number of discrete levels. Since for small values of n, i.e., for $n \ll n_0$, the deviation of the potential field (4.14) from the Coulomb field can be neglected in the leading approximation, and the use of the quasiclassical method in the case of the Coulomb field yields an exact result, the total number $\mathscr{N}$ of discrete levels for $n_0 \gg 1$ can be found, using the quasiclassical formula[1]:

$$\mathscr{N} = -\frac{m}{4\hbar^2} \int U(r) r dr = \frac{Z}{4} \frac{r_D}{a_B} = \left(\frac{n_0}{2}\right)^2. \tag{4.19}$$

In this case there are no bound states with $n \gg n_0$. As the density of the surrounding ionized gas increases, the number $\mathscr{N}$ of discrete levels decreases, and the spectral lines corresponding to the transitions from the highest levels disappear. The value of n_0 in a dense laser plasma with $N_e \approx 10^{24}$ cm^{-3} and $T = 750$ eV turns out to be rather small when $Z = 10$ (Ref. 14): $n_0 \sim 6$. In a superdense plasma, for which $r_D \leqslant a_B/Z$, a nucleus with charge Z loses completely all its discrete electron levels as a result of the electrostatic screening, i.e., $\mathscr{N} = 0$ in this case.

Thus far, we have been interested only in the purely classical nonlocal effects of the long-range correlation between the bound electron and the particles of the surrounding plasma. On the other hand, a definite contribution to the level energy is made also by the essentially quantum local Fermi-liquid-type corrections similar to the corrections considered in Sec. 1, and due to the exchange interaction of the localized electron with the electrons of the plasma background, an interaction which is important for the states with $\bar{r} \gg N^{-1/3}$. For the low-lying states (i.e., for the states with $Z/n \gg 1$), perturbation theory is always applicable to the Coulomb interaction between the bound electron and the free electrons. For high quantum-number values (i.e., for $Z/n \ll 1$), the use of perturbation theory is justified when $T \gg$ Ry. The level shift due to the exchange interaction is then determined by a simple first-order diagram (Fig. 2). In order not to interrupt the discussion, we perform all the calculations in the Appendix, and give only the result here:

FIG. 2.

$$\delta\Sigma_{\alpha\beta} = -\frac{1}{2} \frac{(\hbar\Omega_e)^2}{T} (\delta_{\alpha\beta} + \alpha\sigma_{\alpha\beta}\mathfrak{M}), \quad \Omega_e^2 = \frac{4\pi e^2 N_e}{m}. \tag{4.20}$$

In (4.20) the first term gives the level shift, while the second term gives the level splitting if by chance the system of plasma electrons is magnetically polarized with degree of polarization α. The distance between the components of the Zeeman doublet will also change to the same extent (see Sec. 1).

The energy of a free electron of the plasma background also change in proportion to these same exchange corrections:

$$\delta\Sigma_{\alpha\beta}^{(f)} = \frac{1}{4\pi^{1/2}} \frac{(\hbar\Omega_e)^2}{T} F\left(\frac{p^2}{2mT}\right) (\delta_{\alpha\beta} + \alpha\sigma_{\alpha\beta}\mathfrak{M}), \quad F(z) = \int_{-\infty}^{\infty} \frac{\exp(-x^2) dx}{x^2 - z}, \tag{4.21}$$

which is now a complicated function of the momentum p. The function $F(z)$ can be expressed in terms of the probability integral $w(y)$ of the complex variable:

$$F(z) = \frac{\pi^{1/2}}{2z} [f(z^{1/2}) + f(-z^{1/2})], \quad f(y) = \frac{y}{\pi^{1/2}} \int_{-\infty}^{\infty} \frac{\exp(-z^2) dz}{z - y} = i\pi^{1/2} y w(y). \tag{4.22}$$

For high momentum values, i.e., for $p^2 \gg mT$, the exchange correction (4.21) to the energy is proportional to p^{-2}:

$$\delta\Sigma_{\alpha\beta}^{(f)} = -2\pi(\hbar/p)^2 e^2 N_e (\delta_{\alpha\beta} + \alpha\sigma_{\alpha\beta}\mathfrak{M}), \quad p^2 \gg mT,$$

and for $\hbar/a_B \ll p \ll (mT)^{1/2}$ the expression (4.22) coincides with (4.20). The correction (4.21) to the free-electron energy also affects the macroscopic equations for the self-consistent field, i.e., it also makes its own contribution to the shift of the bound-electron level. For the states in which $N_e^{-1/3} \ll \bar{r} \ll r_D$, this indirect contribution is, however, proportional to a product of two small parameters: $(\bar{r}/r_D) \cdot (\mathrm{Ry}/T) \ll 1$, and therefore turns out to be significantly smaller than the direct exchange correction (4.20) for the bound electron. Thus, allowance for the correction (4.20) together with (4.12) does not go beyond the needed accuracy, and we can write

$$\Delta E = Ze^2/r_D - (\hbar\Omega_e)^2/2T. \tag{4.23}$$

Notice that the contribution of the effects of the interaction of the bound electrons with the plasma background to the level energies of many-electron ions can be more important than the shift due to the interaction of the bound electrons with each other.

5. INSTABILITIES. PHASE TRANSITIONS, HIGH-FREQUENCY OSCILLATIONS

Let us investigate the stability of a gaseous medium of neutral particles, in which a system of highly-excited atoms has been placed, so that the condition (1.1) is fulfilled. The free energy of each of the components is given by the well-known formula of statistical physics[17]:

$$F_i=-N_iT\ln\left[\frac{e}{N_i}\left(\frac{M_iT}{2\pi\hbar^2}\right)^{3/2}\sum_m \exp(-\varepsilon_m/T)\right],\quad i=1,2. \tag{5.1}$$

Assuming for simplicity that the atoms of the medium are in the ground state, while all the excited atoms are in a definite state $|n\rangle$ (the excitation is effected by means of resonance radiation, for example), we find with the aid of (1.15) the total free energy F:

$$F=-T\sum_{i=1}^{2}N_i\ln\left[\frac{eg_i}{N_i}\left(\frac{M_iT}{2\pi\hbar^2}\right)^{3/2}\right]+N_1\varepsilon_{01}-N_2\mathscr{E}_{0n}+\left(8\pi\varkappa\mathscr{E}_{0n}+\frac{\pi\hbar^2}{2m}a_1\right)N_1N_2, \tag{5.2}$$

where the subscript $i=1$ pertains to the medium, $i=2$ pertains to the system of excited atoms, and g_i is the statistical weight. In (5.2) we have dropped the virial corrections that are quadratic in N_i, which are due to the interaction of the heavy atoms with each other, since even at very low temperatures they contain the small factor $m/M_i \ll 1$ in comparison with the last term in (5.2). Allowance for such virial corrections does not present any difficulties; it only makes the subsequent computations tedious. The thermodynamic condition for the system to be stable is violated if

$$\det\|\partial^2F/\partial N_i\partial N_k\|\leqslant 0. \tag{5.3}$$

From (5.3) we find with the aid of (5.2) the critical temperature T_c upon the attainment of which the given two-component system of unexcited and excited atoms becomes unstable:

$$T_c=|G|(N_1N_2)^{1/2},\quad G=8\pi\varkappa\mathscr{E}_{0n}+\pi\hbar^2a_1/2m. \tag{5.4}$$

The use of the formulas of the Boltzmann statistics is justified if $T_c \gg \varepsilon_{di}$ $(i=1,2)$, where ε_{di} is the quantum-degeneracy temperature. It is not difficult to see that, because of the smallness of $m/M_i \ll 1$, there always exist ranges of N_1 and N_2 values where the condition $T_i \gg \varepsilon_{di}$ is fulfilled. Thus, at high values of n this condition is fulfilled if

$$1\gg\gamma_1\gg(m/M_2)(M_2/M_1)^{1/4},\quad 1\gg\gamma_2\gg(m/M_1)(M_1/M_2)^{1/4},\quad \gamma_i=N_i^{1/3}|a_1|,\ i=1,2. \tag{5.5}$$

The above-considered instability can occur if the usual first-order phase transition connected with the condensation into the liquid phase of one or both components does not occur at $T > T_c$ as the temperature is lowered, i.e., if

$$\mu_i^{(G)}(N_i,T)<\mu_i^{(L)}(N_i,T)$$

at $T \geqslant T_c$, or

$$N_i<2(M_iT_c/2\pi\hbar^2)^{3/2}\exp(-|\mu_i^{(L)}|/T_c), \tag{5.6}$$

where $\mu_i^{(G)}$ and $\mu_i^{(L)}$ are the chemical potentials for the gaseous and liquid phases respectively. Unfortunately, the experimental observation of such an instability in an excited gas meets with certain difficulties, since, in order for the T_c not to be too low, it is necessary that the pressure of the medium be high, i.e., that $N_1 \sim 10^{21}$ cm^{-3}, and the highly excited atoms be of equally high concentration $N_2 \sim 10^{20}$ cm^{-3} and have a lifetime longer than the relaxation time τ. In charged-particle systems (a cold plasma, the electron gas in a semiconductor), the development of a similar instability leads to the appearance of a charge-density wave.[13,18]

Treating the interaction of an atom in the ground state with a highly excited atom as scattering on a compound particle (similarly to the scattering of neutrons by molecules), we can easily verify that, as in Refs. 13 and 18, there appear in the kinematic part of the kinetic equations for the two components a Fermi-liquid-type gradient correction due to the mutual zero-angle scattering of a particle of the medium and an optical electron in an excited atom:

$$\begin{gathered}(\omega-\mathbf{kv}_1)\delta n_1+\mathbf{k}\frac{\partial n_1}{\partial\mathbf{p}}u_0\sum_{\mathbf{p}}\delta n_2=0,\quad \mathbf{v}_i=\frac{\mathbf{p}}{M_i},\ i=1,2,\\ (\omega-\mathbf{kv}_2)\delta n_2+\mathbf{k}\frac{\partial n_2}{\partial\mathbf{p}}u_0\sum_{\mathbf{p}}\delta n_1=0,\quad u_0=\frac{\pi\hbar^2a_1}{2m}.\end{gathered} \tag{5.7}$$

The eigenvalues of the system of collisionless kinetic equations (5.7) give the dispersion law $\omega(\mathbf{k})$ for the high-frequency $(\omega\tau \gg 1)$ vibrations of the zero-sound type with $|\omega| \gg kv_{Ti}$, where $v_{Ti}=(T/M_i)^{1/2}$ is the thermal velocity:

$$\omega^2=(N_1N_2/M_1M_2)^{1/2}u_0k^2. \tag{5.8}$$

From the consistency of the conditions $|\omega| \gg kv_{Ti}$ and $T > T_c$ we find the inequality

$$|G|\ll\hbar^2|a_1|/m, \tag{5.9}$$

upon the fulfillment of which weakly-damped high-frequency density oscillations can propagate in the excited gas. Actually, the inequality (5.9) is equivalent to the conditions

$$(\hbar^2/m)|a_1|(n+\Delta_l)^2/\varkappa\ll\mathrm{Ry},\quad a_1<0. \tag{5.10}$$

If the photoexcitation of the atoms occurred in a spin-polarized gas, then the excited two-component system can also propagate high-frequency spin waves with a quadratic dispersion law, which in this case formally coincides with the spectrum of the magnetization intensity oscillations in a weakly ionized gas[13]:

$$\omega=-\frac{2\beta H}{\hbar}-\frac{\Omega_1\Omega_2}{\Omega_1+\Omega_2}\left(\frac{k^2v_{T1}^2}{\Omega_2^2}+\frac{k^2v_{T2}^2}{\Omega_1^2}\right),\quad \Omega_i=\frac{2\pi\hbar a_2}{m}N_i\alpha_i, \tag{5.11}$$

$$\omega=-\frac{2\beta H}{\hbar}+\Omega_1+\Omega_2+\frac{\Omega_1\Omega_2}{\Omega_1+\Omega_2}\left(\frac{k^2v_{T1}^2}{\Omega_1^2}+\frac{k^2v_{T2}^2}{\Omega_2^2}\right). \tag{5.12}$$

If the magnetic polarization of the system was produced through the injection of spins, then we must set $\mathbf{H}=0$ in the formulas (5.11) and (5.12). At $\mathbf{k}=0$ the expressions (5.11) and (5.12) yield two electron-paramagnetic-resonance frequencies in accordance with the two types of uniform oscillations of the magnetic moments of the subsystems.[13]

The experimental observation of such effects is significantly easier in semiconductors with shallow impurity levels and point magnetic defects provided that $\bar{r} \gg N_d^{-1/3}$ (see Sec. 3). There will occur in such a semiconductor at a sufficiently low temperature a phase transition connected with the magnetic ordering of the impurity levels and the point defects. All the calculations here turn out to be the same as in the case of the interaction of a gas of free electrons with magnetic point defects.[13] Indeed, the magnetic free energy of the semiconductor in the present case has the same form as the corresponding energy in Ref. 13:

$$F_M=\frac{M_i^2}{2\chi^{(0)}N_i}+\frac{M_d^2}{2\chi^{(0)}N_d}+\frac{\pi\hbar^2}{2m\beta^2}a_2\mathbf{M}_i\mathbf{M}_d,\quad \chi^{(0)}=\frac{\beta^2}{T}, \tag{5.13}$$

where $\mathbf{M}_i$ and $\mathbf{M}_d$ are respectively the magnetizations of the impurity-level and defect systems and N_i is the number of impurity levels in a unit volume.

The minimization of the free energy (5.13) enables us to find the critical temperature of the ferromagnetic, $\mathbf{M}_i \uparrow\uparrow \mathbf{M}_d$ (when $a_2 > 0$), ordering:

$$T_c=(\pi\hbar^2/2m)\,|a_2|\,(N_iN_d)^{1/2}. \tag{5.14}$$

At $T > T_c$ the detection of the double EPR signals,

$$\omega=-\frac{2\beta H}{\hbar},\quad \omega=-\frac{2\beta H}{\hbar}+\frac{2\pi a_2\hbar}{m}(N_d+N_i)\,\mathrm{th}\,\frac{\beta H}{T}, \tag{5.15}$$

is experimentally possible even when the number of impurity levels is relatively small. At $T < T_c$ it is also experimentally possible to observe a homogeneous antiferromagnetic resonance at a frequency equal to

$$\omega=(2\pi\hbar a_2/m)\,(N_i\alpha_i\pm N_d\alpha_d), \tag{5.16}$$

where the plus sign corresponds to the ferromagnetic order, the minus sign corresponds to the ferrimagnetic type of structure, and the equilibrium values of the degrees of polarization α_i and α_d are, when allowance is made for the fact that $N_d \gg \bar{r}^{-3} \gg N_i$, given by the following expressions:

$$\begin{gathered}\alpha_i=(6\tau)^{1/2},\quad \alpha_d=\left(\frac{N_i}{N_d}\right)^{1/2}\alpha_i,\quad \tau\equiv\frac{T_c-T}{T_c}\ll 1;\\ \alpha_i=1-\exp\left[-2\left(\frac{T_c}{T}\right)^2\right],\quad \alpha_d=\frac{T_c}{T}\left(\frac{N_i}{N_d}\right)^{1/2},\quad \left(\frac{N_i}{N_d}\right)^{1/2}\ll\frac{T}{T_c}\ll 1;\\ \alpha_i=1-\exp\left[-2\frac{T_c}{T}\left(\frac{N_d}{N_i}\right)^{1/2}\right],\ \alpha_d=1-\exp\left[-2\frac{T_c}{T}\left(\frac{N_i}{N_d}\right)^{1/2}\right],\ \frac{T}{T_c}\ll\left(\frac{N_i}{N_d}\right)^{1/2},\end{gathered} \tag{5.17}$$

i.e., the inequality $N_d\alpha_d \gg N_i\alpha_i$ is always fulfilled.

The author is grateful to A. F. Andreev for a thorough discussion of the results of the paper and to the participants of I. I. Sobel'man's seminar for a useful and important discussion.

APPENDIX

The electron–electron interaction Hamiltonian has the form

$$\hat{H}_{int}=\frac{1}{2}\int\hat{\Psi}^+(\mathbf{r}_1)\hat{\Psi}^+(\mathbf{r}_2)\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}\hat{\Psi}(\mathbf{r}_2)\hat{\Psi}(\mathbf{r}_1)\,d\mathbf{r}_1d\mathbf{r}_2, \tag{A1}$$

where the field operators $\hat{\Psi}(\mathbf{r})$ and $\hat{\Psi}^+(\mathbf{r})$ can be expressed in terms of the creation and annihilation operators $\hat{a}_\alpha^+$ and $\hat{a}_\beta$ for the electrons in the usual manner:

$$\hat{\Psi}(\mathbf{r})=\sum_i\psi_{i\alpha}(\mathbf{r})\,\hat{a}_{i\alpha},\quad \hat{\Psi}^+(\mathbf{r})=\sum_k\psi_{k\beta}^*(\mathbf{r})\,\hat{a}_{k\beta}^+. \tag{A2}$$

In (A2) the Latin and Greek subscripts number respectively the orbital and spin states, summation over repeated spin indices is implied, and $\psi_{i\alpha}(\mathbf{r})$ is the wave function describing the state $|i\alpha\rangle$.

Let us substitute (A2) into the expression (A1), and compute the mean value $\langle\hat{H}_{int}\rangle = E_{int}$. Performing the averaging with the aid of Wick's theorem, and taking into account the fact that the Coulomb interaction is spin independent, we finally find the contribution of the exchange effects to the total interaction energy:

$$\begin{gathered}E_{int}^{(ex)}=-\frac{1}{2}\sum_{lm}U_{lm}^{ml}\,n_{\alpha\beta}^{(l)}\,n_{\beta\alpha}^{(m)},\\ U_{lm}{}^{ki}=\int\psi_i^*(\mathbf{r}_1)\psi_k^*(\mathbf{r}_2)\frac{e^2}{|r_1-r_2|}\psi_l(\mathbf{r}_2)\psi_m(\mathbf{r}_1)\,d\mathbf{r}_1d\mathbf{r}_2,\end{gathered} \tag{A3}$$

where we have introduced the polarization density matrix

$$\langle\hat{a}_{i\alpha}{}^+\hat{a}_{k\beta}\rangle=n_{\alpha\beta}^{(i)}\,\delta_{ik}, \tag{A4}$$

and the matrix element $U_{lm}{}^{ml}$ is computed with the purely orbital wave functions $\psi_k(\mathbf{r})$.

Varying $E_{int}^{(ex)}$ from (A3) with respect to $n_{\beta\alpha}^{(k)}$, and taking into account the fact that, because of the isotropy in the system, $U_{km}{}^{mk} = U_{mk}{}^{km}$, we obtain the correction to the electron energy, that stems from the electron–electron exchange interaction:

$$\delta\Sigma_{\alpha\beta}^{(k)}=\frac{\delta E_{int}^{(ex)}}{\delta n_{\beta\alpha}^{(k)}}=-\sum_m n_{\alpha\beta}^{(m)}U_{km}^{mk}. \tag{A5}$$

Assuming that the state $|k\rangle$ describes the localized electron, while all the states $|m\rangle$ pertain to the free electrons of the plasma background, we have in first order the expression

$$U_{km}^{mk}=e^2\int\frac{\exp[i\mathbf{k}(\mathbf{r}_1-\mathbf{r}_2)]}{|\mathbf{r}_1-\mathbf{r}_2|}\psi_{k0}^*(\mathbf{r}_1)\psi_{k0}(\mathbf{r}_2)\,d\mathbf{r}_1d\mathbf{r}_2, \tag{A6}$$

where $\hbar\mathbf{k} = \mathbf{p}$, $n_{\alpha\beta}^{(m)} \equiv n_{\alpha\beta}(\mathbf{p})$ is given by the formulas (1.3)–(1.6) for the electrons, and the ψ_{k0} are the unperturbed hydrogenic functions from (4.2).

Let us set $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$, $2\mathbf{R} = \mathbf{r}_1 + \mathbf{r}_2$ in (A6), and perform the integration over the angle between the vectors $\mathbf{k}$ and $\mathbf{r}$. The single integration by parts with allowance made for the relation $k\bar{r} \gg 1$ leads to the result

$$\begin{aligned}U_{km}^{mk}=\frac{e^2}{ik}\int d\mathbf{R}\,dr\,d\varphi_r\Big\{&e^{ikr}\psi_{k0}^*\left(\mathbf{R}-\frac{\mathbf{r}}{2}\right)\psi_{k0}\left(\mathbf{R}+\frac{\mathbf{r}}{2}\right)\Big|_{\theta_r=0}\\ &-e^{-ikr}\psi_{k0}^*\left(\mathbf{R}-\frac{\mathbf{r}}{2}\right)\psi_{k0}\left(\mathbf{R}+\frac{\mathbf{r}}{2}\right)\Big|_{\theta_r=\pi}\Big\}+O\left(\frac{1}{k\bar{r}}\right).\end{aligned} \tag{A7}$$

Now integrating (A7) by parts with the use of the normalization condition

$$\int|\psi_{k0}(\mathbf{R})|^2d\mathbf{R}=1 \tag{A8}$$

for the wave functions of the bound electron, we find

$$U_{km}{}^{mk}=4\pi e^2\hbar^2/p^2+O(1/k^2). \tag{A9}$$

Substituting (A9) and (1.4) into (A5), we arrive at the formula (4.20), which is valid at high temperatures. If by chance the temperature is so low that the atomic velocity of the bound electron is significantly higher than the thermal velocity for the free-electron gas, then

$$\delta\Sigma_{\alpha\beta}^{(k)}=-{}^1/_2N_eU_{k0}^{0k}(\delta_{\alpha\beta}+\alpha\sigma_{\alpha\beta}\mathfrak{M}), \tag{A10}$$

where $U_{k0}{}^{0k}$ is given by the formula (A6) with $\mathbf{k} = 0$. If the state $|k\rangle$ pertains also to the free electron, then

$$U_{km}{}^{mk}=4\pi e^2\hbar^2/(\mathbf{p}-\mathbf{p}')^2 \tag{A11}$$

and, performing the exact integration, we obtain the expression (4.21).

[1] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics), Nauka, Moscow, 1974 (Eng. Transl., Pergamon Press, Oxford, 1977), p. 677.
[2] E. Fermi, Nuovo Cimento **11**, 157 (1934).
[3] O. B. Firsov, Zh. Eksp. Teor. Fiz. **21**, 627, 634 (1951).
[4] V. A. Alekseev and I. I. Sobel'man, Zh. Eksp. Teor. Fiz. **49**, 1274 (1965) [Sov. Phys. JETP **22**, 882 (1966)].
[5] M. A. Mazing and N. A. Vrublevskaya, Zh. Eksp. Teor. Fiz. **50**, 343 (1966) [Sov. Phys. JETP **23**, 228 (1966)].
[6] M. A. Mazing and P. D. Serapinas, Zh. Eksp. Teor. Fiz. **60**, 541 (1971) [Sov. Phys. JETP **33**, 294 (1971)].
[7] G. F. Drukarev, Stolknoveniya élektronov s atomami i molekulami (Collisions of Electrons with Atoms and Molecules), Nauka, Moscow, 1978, p. 180.
[8] V. S. Édel'man, Usp. Fiz. Nauk **130**, 675 (1980) [Sov. Phys. Usp. **23**, 227 (1980)].
[9] L. D. Landau and E. M. Lifshitz, Élektrodinamika sploshnykh sred (Electrodynamics of Continuous Media), Fizmatgiz, Moscow, 1959 (Eng. Transl., Pergamon Press, Oxford, 1960), p. 60
[10] S. Chen and M. Takeo, Rev. Mod. Phys. **29**, 20 (1957) (Russ. Transl., Usp. Fiz. Nauk **66**, 391 (1958)].
[11] C. C. Grimes, T. R. Brown, M. L. Burns, and C. L. Zipfel, Phys. Rev. B **13**, 140 (1976).
[12] A. P. Volodin and V. S. Édel'man, Zh. Eksp. Teor. Fiz. **81**, 368 (1981) [Sov. Phys. JETP **54**, (1981)]; Pis'ma Zh. Eksp. Teor. Fiz. **30**, 668 (1979) [JETP Lett. **30**, 633 (1979)].
[13] E. P. Bashkin, Zh. Eksp. Teor. Fiz. **82**, 254 (1982) [Sov. Phys. JETP **55**, 152 (1982)].
[14] S. Skupsky, Phys. Rev. A **21**, 1316 (1979).
[15] E. M. Lifshitz and L. P. Pitaevskiĭ, Fizicheskaya kinetika (Physical Kinetics), Nauka, Moscow, 1979 (Eng. Transl., Pergamon Press, Oxford, 1981), p. 182.
[16] S. Flügge, Practical Quantum Mechanics, Vol. 1, Springer Verlag, Berlin, 1971 (Russ. Transl., Mir, Moscow, 1974, p. 198).
[17] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Chast' 1, Nauka, Moscow, 1976 (Eng. Transl., Vol. 1, Pergamon Press, Oxford, 1980).
[18] E. P. Bashkin, Pis'ma Zh. Eksp. Teor. Fiz. **33**, 11 (1981); **34**, 86 (1981) [JETP Lett. **33**, 8 (1981); **34**, 81 (1981)].

Translated by A. K. Agyei