Inelastic autoionization of quasimolecules and the Penning effect

F. I. Dalidchik

Institute of Chemical Physics, USSR Academy of Sciences
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We discuss in the adiabatic approximation the exchange interaction of a metastable atom with a hydrogenlike atom and with an atom having two electrons above the filled shells. An analysis is made of the mechanisms of inelastic autoionization of quasimolecules, i.e., ionization accompanied by formation of an electronically excited quasimolecular ion. Formulas are obtained for the widths, and the cross sections for inelastic and two-electron Penning ionization are evaluated. A relation is established between the asymmetry of the electron angular distribution and the elastic scattering of atoms. The complex quantum effect of quasimolecular Rydberg crowding is calculated in terms of a model of interacting scattering centers, with account taken of the existence of a pseudocrossing in the ionic term system. The effect of exchange interaction on the probability of a nonadiabatic transition between decaying states is discussed.

1. The Penning effect, i.e., ionization of an atomic particle A in a thermal collision with an excited atom B* (for the condition that the excitation energy of atom B*, ω_B, exceeds the ionization potential of particle A, ϵ_A):

$$A+B^*\to A^++e+B, \tag{1}$$

plays an important role in many phenomena of the physics of low temperature plasma. The cross sections for ionization by metastable helium atoms, for example, in many cases reach values[1] of the order 10^{-15}–10^{-14} cm^2. Process (1) is responsible for the variation of the concentration of charged particles in a decaying plasma,[2] substantially affects the afterglow of gases in radiolysis, photolysis, passage of shock waves, and so forth. A process close to (1)–de-excitation of a mesic atom B_π as the result of ionization of atomic particles–plays an important role in the dynamics of excited states of mesic molecules.[3] In recent years Penning spectroscopy has been successfully developed, i.e., spectroscopy of quasimolecular states, based on measurement of the energy spectra and angular distributions of the liberated electrons.[4-7]

The theoretical basis of work on Penning spectroscopy is the representation of process (1) as the autoionization of quasimolecules, accompanied by a vertical electronic transition from the decaying state AB* (the term U*(R)) to one of the states of the electronic continuum whose lower limit is the ground term of the quasimolecular ion AB^+ ($U^+(R)$) (Fig. 1). In the semiclassical approximation according to this representation the cross section for process (1) and the electron spectrum n(E) can be found after summation over the impact parameters ρ respectively of the total probability $P(\rho)$ and differential probability $P(E, \rho)$ for ionization of the quasimolecule:[6, 7]

$$\sigma=2\pi\int_0^\infty P(\rho)\rho\,d\rho, \tag{2}$$

$$n(E)=2\mu W\int_0^\infty P(E,\rho)\rho\,d\rho. \tag{3}$$

Here W is the energy of relative motion of the nuclei, μ is the reduced mass, e = h = m = 1,

$$P(\rho)=\int_{R_{min}(\rho)}^\infty P(R,\rho)\,dR, \tag{4}$$

$$P(R,\rho)=\frac{2\Gamma(R)}{v(\rho,R)}\exp\left(-\int_{R_{min}(\rho)}^\infty\frac{\Gamma(R)\,dR}{v(\rho,R)}\right)\mathrm{ch}\left(\int_{R_{min}(\rho)}^\infty\frac{\Gamma(R)\,dR}{v(\rho,R)}\right), \tag{5}$$

$$P(E,\rho)=\sum_i P_i(R_i,\rho)\left|\frac{d}{dR}(U^*(R)-U^+(R))\right|^{-1}_{R=R_i(E)}. \tag{6}$$

Here $R_{min}(\rho)$ is the classical turning point, $v(\rho, R)$ is the radial velocity of relative motion of the nuclei, and $R_i(e)$ are the roots of the equation

$$U^*(R)-U^+(R)=E \tag{7}$$

(E is the energy of the liberated electron). The cross section and the spectrum are determined first of all by the probability of an electronic transition per unit time $\Gamma(R)$ (the autoionization width), calculation of which comprises the central problem of the theory.[1)] For a resonance-excited atom B* the exchange of energy with particle A leading to removal of an electron is due to the long range dipole-dipole interaction. In this case $\Gamma\sim R^{-6}$ and is expressed in terms of the characteristics of the corresponding optical transitions of the isolated atoms: the radiative transition to the ground state of atom B and photoionization of atom A.[1, 9-11] However, as a result of the small lifetime of resonance excited states, this process has not yet been observed experimentally, and all data obtained up to the present time on Penning ionization refer to metastable atoms B^m. In these cases the exchange interaction is responsible for the autoionization and

$$\Gamma\sim\exp[-\sqrt{-2\varepsilon_A}R]. \tag{8}$$

The dependence (8) is directly confirmed by analysis of the experimental spectra[12] and by the results of the few calculations which exist for the simplest systems (HHe^m and He^mHe^m).[13-14] For metastable atoms of the inert gases, which have rather high excitation energies (~10–20 eV), in addition to elastic Penning ionization (1), inelastic ionization is also energetically possible, i.e., ionization accompanied by formation of the excited atom A_n^+ (refs. 15–17) (n is the index of the excited state of the ion):

$$A+B^m\to A_n^++e+B \tag{9}$$

or by removal of two electrons at once:[17]

$$A+B^m\to A^{++}+2e+B. \tag{10}$$

Processes (9) and (10) not only present great practical interest (process (9), for example, explains the forma-

tion of a population inversion of the levels in continuously acting lasers operating in vapors of alkaline earth metals[18-19]), but also broadens substantially the possibilities of Penning spectroscopy. These processes are being intensively studied at the present time experimentally, but up to this time they have not been discussed theoretically. Analysis of the mechanisms of inelastic Penning ionization is the main content of the present article.

2. If in a system of terms $U^+(R)$, $U_n^+(R)$ (the ground state and n-th excited state of the quasimolecular ion), $U^{a.i.}(R)$ (the term correlating at infinity with autoionization of the level of the atom A), and $U^m(R)$ (correlating at infinity with the initial metastable state of the atom B^m) there is no pseudocrossing, i.e., for all internuclear distances the following condition is satisfied,

$$U^+(R)<U_n^+(R)<U^m(R)<U^{a.i.}(R), \tag{11}$$

then the main mechanism of process (9) and (10) is inelastic autoionization of the quasimolecule, i.e., a vertical electronic transition to levels of the corresponding continua whose lower limits are the terms $U_n^+(R)$ (Fig. 2). The cross section and spectrum in this case are described by Eqs. (2)–(6) with replacement in the preexponential factors of the total width $\Gamma(R)$ by the partial widths $\Gamma_f(R)$ which determine the final state of the system.

Turning our attention below to cases of hydrogenlike atoms and atoms with two electrons above filled shells (atoms A), for the probability of inelastic autoionization accompanied by emission of an electron in the direction of the vector **k** and by a formation of an ion A^+ in the n-th state ($f \equiv (\mathbf{k}, n)$), we have in the leading approximation

$$\Gamma_f = d\Gamma_n/d\Omega_k = \sqrt{2E}\,|M_n(\mathbf{k})|^2, \tag{12}$$

$$M_n(\mathbf{k}) = \int d\xi\, d\mathbf{r}_1\, d\mathbf{r}_2 \Phi_A^*(\mathbf{r}_1\xi)\varphi_{Bm}^*(\mathbf{r}_2) V_{12}\varphi_{B0}(\mathbf{r}_1)\Psi_{n,k}^{(-)}(\mathbf{r}_2,\xi). \tag{13}$$

Here V_{12} is the interelectron interaction; $\Phi_A(\mathbf{r}_1\xi)$ is the wave function of atom A in the initial state ($\mathbf{r}_1$ is the coordinate of the electron being exchanged); $\varphi_{Bm}(\mathbf{r}_2)$ is the wave function of the electron of the metastable atom B^m; φ_{B0} is the wave function of the electron in the ground state of atom B; $\Psi_{n,k}^{(-)}$ is the wave function of the system in the final state, i.e., the eigenfunction of the Hamiltonian

$$H_{AB}(\mathbf{r},\xi) = -\tfrac{1}{2}\Delta_r + H_{A^+}(\xi) + V_{eA^+} + V_{eB0}. \tag{14}$$

Here $H_{A^+}(\xi)$ is the Hamiltonian of the atomic ion A^+; V_{eB0} and V_{eA^+} are the interaction of the electron with the unexcited atom B and with the ion A^+, respectively.

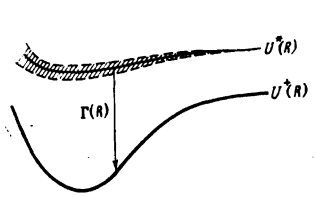

FIG. 1

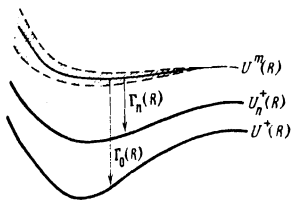

FIG. 2

FIG. 1. Autoionization of quasimolecules (see explanations in text).

FIG. 2. Channels of elastic autoionization $\Gamma_0(R)$ and inelastic autoionization $\Gamma_n(R)$ of a quasimolecule (see explanations in text).

The wave function $\Psi_{n,k}^{(-)}$ satisfies the Lippman-Schwinger equation:

$$\Psi_{n,k}^{(-)} = F_n(\xi)\exp\{i\mathbf{k}_n\mathbf{r}\} + G_0^{(-)}(V_{eA^+} + V_{eB0})\Psi_{n,k}^{(-)}, \tag{15}$$

i.e., has a converging spherical wave at infinity. The Green's function of the free electron and ion has the form

$$G_0^{(-)} = \left(E + \frac{\Delta}{2} - H_{A^+}\right)^{-1} = \sum_n F_n^*(\xi)F_n(\xi)\frac{\exp\{-ik_n|r-r'|\}}{2\pi|r-r'|}, \tag{16}$$

$$k_n^2/2 = \omega_B - \varepsilon_A - \omega_{A^+n}, \tag{17}$$

ω_{A^+n} is the excitation energy of the ion ($\omega_{A^+} = 0$), and $F_n(\xi)$ is the corresponding wave function of the ion.

Effects of multiple scattering of the electron in atom B are unimportant in the case considered. Their contribution is of order l/R (l is the amplitude for scattering of the electron in atom B), i.e., of the order 0.1; these effects are not considered below. If necessary the corresponding corrections can be found.[20, 21]

In the single-particle approximation

$$\Phi_A(\mathbf{r},\xi) = \Phi(\mathbf{r})F(\xi), \tag{18}$$

$$M_n(\mathbf{k}) = M_n^{(1)}(\mathbf{k}) + M_n^{(2)}(\mathbf{k}), \tag{19}$$

$$M_n^{(1)}(\mathbf{k}) = \langle F|F_n\rangle \int d\mathbf{r}_1 d\mathbf{r}_2 \Phi^*(\mathbf{r}_1)\varphi_{Bm}^*(\mathbf{r}_2)V_{12}\varphi_{B0}(\mathbf{r}_1)\Psi_{Ck_n}^{(-)}(\mathbf{r}_2), \tag{20}$$

$$M_n^{(2)}(\mathbf{k}) = \sum_{n'}\langle F|F_{n'}\rangle \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_2' d\xi\, \Phi^*(\mathbf{r}_1)\varphi_{Bm}^*(\mathbf{r}_2)\cdot$$

$$\cdot F_{n'}^*(\xi)V_{12}G_C^{(-)}(\mathbf{r}_2,\mathbf{r}_2',E_{n'})u_{eA^+}\Psi_{nk_n}^{(-)}(\mathbf{r}_2',\xi'). \tag{21}$$

Here $\Psi_{Ck_n}^{(-)}$ is the Coulomb wave function of the electron in the field of the ion A^+, which has a converging spherical wave in the asymptote, $G_C^{(-)}$ is the Coulomb Green's function, u_{eA^+} is the nondiagonal (in the ion states) part of the total electron-ion interaction ($u_{eA^+} - 1/r = V_{eA^+}$).

The two separated terms correspond to two different mechanisms of inelastic autoionization of the quasimolecule. The first term, which is important for strong correlation of the electrons in atom A, corresponds to the possibility of direct inelastic autoionization, i.e., excitation of the ion A^+ at the moment of a sudden change in the selfconsistent potential of atom A due to removal of an electron. The second term, $M_n^{(2)}$, corresponds to excitation of the ion on secondary scattering in it of the electron liberated at the moment of de-excitation of the metastable atom B^m. An exact calculation of $M_n^{(1)}(\mathbf{k})$ and $M_n^{(2)}(\mathbf{k})$ with the use of many-electron wave functions is possible only for the simplest system.[13, 14]

If the conditions

$$R \gg 1, \quad R\sqrt{\varepsilon_{Bm}} \gg 1, \quad (\varepsilon_A/\varepsilon_{B0})^{1/2} \ll 1 \tag{22}$$

are satisfied (ϵ_{Bm} and ϵ_{B0} are the ionization potentials of atom B respectively in the metastable and ground states) the matrix elements (20) and (21) permit substantial simplifications in general form. For atomic systems in typical cases $R \sim 7$–10, $R\sqrt{\epsilon_{Bm}} \sim 5$–$7$, and $(\epsilon_A/\epsilon_{B0})^{1/2} \sim 0.5$–$0.3$. For excited, for example, metastable[22] atoms A, the conditions (22) are better satisfied. It should also be noted that the basic formulas obtained below in this section as a particular case contain results applicable to processes of destruction of negative ions by metastable atoms:

$$A^- + B^m \to A + e + B.$$

As a rule the conditions (22) are well satisfied for ionic systems.

For the pair H^-He^m, for example, we have the parameter $(\epsilon_A^-/\epsilon_{B0}) \sim 0.15$. If the conditions (22) are satisfied, it is easy to obtain for the first term (see the similar derivation for the level shift, carried out in ref. 23).

$$M_n^{(1)}(\mathbf{k}) = \langle F_n | F \rangle g^n \Phi(R) \Psi_{C,\mathbf{k}_n}^{(-)}(\mathbf{R}). \tag{23}$$

Here $\mathbf{R} = (\mathbf{R}_B - \mathbf{R}_A)$ is the radius vector of atom B relative to atom A;

$$g^n = \int d\mathbf{r}_1 d\mathbf{r}_2 \varphi_{Bm}^*(\mathbf{r}_2) V_{12} \varphi_{B0}(\mathbf{r}_1) \exp\{-i\mathbf{p}_n\mathbf{r}_2\} \tag{24}$$

is the generalized amplitude for exchange de-excitation of atom B^m by an electron of zero energy ($k_n^2/2 \neq k_0^2/2 = \omega_{Bm}$), $p_n = k_n R/R$. In typical cases $k_n^2 \approx k_0^2$ and $g^n \approx g_0$, i.e., it is close to the physical (experimentally observed) amplitude for breakup of a metastable atom by a slow electron.

In the case discussed the angular distribution of electrons liberated for a fixed location of the nuclei is described by the Coulomb wave function $\Psi_{Ck}^{(-)}$ centered on the nucleus of atom A and taken at the point of location of atom B:

$$N(\theta, R) = \text{const} |F(-i/k, 1, -i(kR + \mathbf{kR}))|^2. \tag{25}$$

We can say that atom B is in effect the "source" of the liberated s electrons.

For small k (in the quasiclassical limit)

$$N(\theta, R) = \text{const} J_0^2\left(2\sqrt{2R\left(1+\frac{\mathbf{kR}}{kR}\right)}\right), \quad k \ll 1. \tag{26}$$

The observed angular distribution of electrons corresponds to the distribution (25) averaged with a weight $\Gamma(R)$ over interatomic distances and impact parameters ρ. The result of this averaging depends substantially on the nature of the elastic scattering of the atoms. Below we will limit ourselves to analysis of two limiting cases, of which one corresponds to the dominant role of attractive forces, and the second to repulsive forces. Taking into account the form of the distributions (25) and (26), it can easily be seen that in the first case the electrons are emitted preferentially into the backward hemisphere (in a direction opposite to the beam of metastable ions B[24]). The dominant role of repulsive forces is felt in the preferential emission of electrons forward (i.e., in the direction of the beam). The asymmetry parameter $\gamma = N(0^\circ_{lab})/N(180^\circ_{lab})$, i.e., the ratio of the number of electrons emitted along the beam to the number of electrons emitted in the opposite direction, can be found in the general case in the approximation of small scattering angles (large impact parameters, which give the main contribution to the cross section of the process). Assuming for the interatomic potential a power function $U^m(R) = a/R^n$, we have

$$\gamma \approx 1 + \frac{a}{W}\left(\alpha_A / \ln\frac{\alpha_A}{v}\right)^n, \quad \alpha_A = (-2\varepsilon_A)^{1/2} \tag{27}$$

(v is the relative velocity of the nuclei). In terms of the opposite model of hard spheres, taking into account that the main contribution in integration over R is from the vicinity of the turning point,[6,7] we have for the observed angular distribution of electrons

$$N(\theta_{lab}) = \text{const} \int_0^{R_0} \rho\, d\rho \int_0^{2\pi} d\varphi J_0^2\left(2^{3/2} R_0^{1/2}\left[1 + \left(1 - \frac{\rho^2}{R_0^2}\right)^{1/2} \cos\theta_{lab} + \frac{\rho}{R_0}\sin\theta_{lab}\cos\varphi\right]^{1/2}\right) \tag{28}$$

(R_0 is the combined radius of the spheres, $R_0 \sim 10$ (ref. 7)).

The asymmetry of the angular distribution arises from the term with $\cos\theta_{lab}$ under the radical sign in the argument of the Bessel function and is retained even as $R_0 \to \infty$. The asymptotic value of γ in this case is $\gamma = 2^{1/2}/(2^{1/2} - 1) \sim 3$. The relative probability of formation of an ion in the n-th excited state is determined in this case by the overlap integral of the wave functions of the "ionic" electrons $F(\xi)$ and $F_n(\xi)$, which can be evaluated independently or reproduced from data on "inelastic" ionization of the atom A by fast electrons:[25-27]

$$e + A \to 2e + A_n^+. \tag{29}$$

The ratio of the inelastic autoionization width Γ_n to the elastic width Γ_0 in this case is equal to the ratio of the cross sections for formation of the excited ion A_n^+ in the process (29) σ_e^n to the cross section for ionization without excitation σ_e^0: $\Gamma_n/\Gamma_0 \sim \sigma_e^n/\sigma_0^n = w^n$. The mechanism discussed provides to the cross section for processes (9) and (10) a contribution $\sim w^n \sigma(1)$, where $\sigma(1)$ is the cross section for elastic Penning ionization (process (1)), which increases logarithmically with decrease of the velocity of collision of the atoms.[1]

For atoms with a weak correlation of the exchanged electron

$$\langle F(\xi) | F_n(\xi) \rangle = \delta_{n0}.$$

The possibility of formation of an excited ion in this case is due to secondary scattering of the electron by the ion A^+ (the term $M_n^{(2)}(\mathbf{k})$). If the conditions (22) are satisfied, we have

$$M_n^{(2)}(\mathbf{k}) = \int d\xi d\mathbf{r}_2 d\mathbf{r}_2' I(\mathbf{r}_2) F_0^*(\xi) G_C^{(-)}(\mathbf{r}_2\mathbf{r}_2' E) u_{eA^+} \Psi_{n,\mathbf{k}_n}^{(-)}(\mathbf{r}_2', \xi), \tag{30}$$

where

$$I(\mathbf{r}_2) = \int d\mathbf{r}_1 \Phi^*(\mathbf{r}_1) \varphi_{Bm}^*(\mathbf{r}_2) V_{12} \varphi_{B0}(\mathbf{r}_1) \approx$$
$$\approx \Phi^*(R) \int d\mathbf{r}_1 \varphi_{Bm}^*(\mathbf{r}_2) V_{12} \varphi_{B0}(\mathbf{r}_1), \quad E = \omega_B - \varepsilon_A.$$

The function $I(\mathbf{r}_2)$ has a maximum in the vicinity of atom B and is exponentially damped at distances of the order $\epsilon_{Bm}^{-1/2}$. The interaction u_{eA^+} nondiagonal in the states of the ion is, on the contrary, maximal in the vicinity of the ion and for optically forbidden transitions (which present special interest[16]) falls off quite rapidly with increasing r_2'.

The main contribution in integration over $\mathbf{r}_2$ and $\mathbf{r}_2'$ in Eq. (30) is from the two nonoverlapping regions of variation of the variables $\mathbf{r}_2$ and $\mathbf{r}_2'$. We can assume that $r_2 > r_2'$ and express $M_n^{(2)}(\mathbf{k})$ in terms of the physical amplitudes for scattering of the electron by ion A^+ and atom B. The accuracy of this approximation, naturally, is greater, the larger R, i.e., the accuracy increases with decreasing velocity of the atoms. Expanding $\Psi_C^{(-)}$ and $G_C^{(-)}$ in spherical functions relative to the center of the ion, we find

$$M_n^{(2)}(k) = \frac{g_0 \Phi^*(R)}{R} \sum_l (2l+1) \chi_l^{(-)}(kR) a_{0n}^l(k) P_l\left(\frac{\mathbf{kR}}{kR}\right). \tag{31}$$

Here g_0 is the amplitude for exchange de-excitation of B^m by a slow electron, $a_{0n}^l(k)$ is the partial amplitude for inelastic scattering of an electron with energy $k^2/2$ by ion A^+, $\chi_l^{(-)}$ is the irregular solution of the radial

Schrödinger equation with a Coulomb potential $\chi^{(-)} \sim e^{ikr}$.

The angular distribution (asymmetric in the general case) depends on the specific values of $a^{l}_{0n}(k)$. The probability of inelastic autoionization and the cross section for inelastic Penning ionization in the ratio σ^{n}_{+}/R_0^2 are less than the cross section for process (1), $R_0 \sim \alpha_A^{-1}\ln(\alpha_A/v)$. Here σ^{n}_{+} is the cross section for excitation of the n-th state of ion A^+ by electron impact

$$e+A^+ \to e+A_n^+. \qquad (32)$$

We will use the results obtained to estimate the role of various mechanisms and the cross sections for processes (9) and (10) occurring in interaction of atoms of the second group with metastable helium atoms.[12, 15-17] The relative yields of various excited states of the ions Zn^+, Cd^+, Hg^+ in process (29) have been given by Hyman.[26] The cross sections for excitation and ionization of positive ions by electron impact are well known.[27] According to these data the probability of single ionization of a divalent atom accompanied by a simultaneous excitation of the second s electron in the closest state nl, i.e., the quantity w^n and, consequently, the contribution of the first mechanism discussed to the cross section for processes of type (9), has the following values: ~5% for $\Delta n = 0$, $l = 1$; ~2% for $\Delta n = 1$, $l = 0$; ~1% for $\Delta n = 0$, $l = 2$; and ~0.1% for $\Delta n = 0$, $l = 3$ of the total cross section for process (1) $\sigma(1) \sim 10^{-15}$ cm^2 (ref. 1). Typical values of the energy $\omega_B - \epsilon_A$ are 10–15 eV. The corresponding cross sections for the processes (30) for ions of divalent atoms have values[27] 10^{-16}–10^{-17} cm^2. For $R_0 \sim$ 5–7 atomic units, this gives $\sigma^{n}_{+}/R_0^2 \sim (2\text{–}5) \times 10^{-2}$.

Thus, the cross sections for processes of inelastic Penning ionization accompanied by minimal change of the quantum numbers of the second valence electron of the atoms Hg, Ca, Sr, and Ba receive commensurate contributions from the two mechanisms discussed. Correspondingly, the cross sections for formation of ^2S_j and ^2P_j ions in process (9) amount to 7–10% of the cross section for process (1). The existing experimental data confirm this conclusion. For mercury, for example, according to the data of ref. 12, the cross section for the process

$$Hg+He^m \to Hg^+(^2P_{1/2})+e+He$$

amounts to 8–15% of the total ionization cross section.

For larger excitations corresponding to larger changes in the quantum numbers of the second electron and to formation of ^2D_j and ^2F_j ions, the contribution of the second mechanism discussed is dominant. Secondary scattering of the electron by the ion A^+ determines also the cross section for two-electron Penning ionization (10) of divalent atoms of the main subgroup Ca, Sr, and Ba. For the Ba atom, for example, the cross section for removal of two s electrons in collision with a metastable helium atom is $\sim 3 \times 10^{-17}$ cm^2 (E ~ 15 eV, the cross section for ionization of Ba^+ by electron impact is $\sigma^{++} \sim 0.7 \times 10^{-16}$ cm^2 (ref. 27), $\sigma(1) \sim 10^{-15}$ cm^2).

The mechanisms discussed for inelastic autoionization of quasimolecules are the main ones at sufficiently large internuclear distances where direct exchange of internal electrons can be neglected. In some cases (for atoms of the secondary subgroups of the second and third group, for example) direct exchange of d electrons, whose "tail" extends appreciably further than the p electrons of the filled shells,[28] may be dominant. In similar cases there is a high probability (~100%) for formation of excited ions corresponding to the presence of a "hole" in the d shell.[12] If the excitation energy of this ion exceeds its ionization potential (this occurs, for example, for Y and Ce), then subsequent Auger ionization leads to formation of the ion A^{++}. The cross section for process (10) in this case should be much greater than that estimated above for Ba, close to characteristic for process (1), i.e., should have a value $\sim 10^{-15}$ cm^2. This also explains the fact that under experimental conditions[17] two-electron Penning ionization has been noted only for Y and Ce.

3. The approach and crossing at small distances of terms of excited states of the quasimolecule with the ground term of the ion (see Fig. 3) leads to an interesting phenomenon recently observed[29] for the atoms Rb and Ar–the Penning effect in collision of unexcited atoms A and B. On close approach, in addition to the ground state of the Penning type AB^m (the term $U^m(R)$) there will also be populated to a comparable degree many excited states which form the Rydberg crowding, whose terms $U^m_n(R)$ at infinity correlate with states of a system of the type $A^*_nB^m$ (here n is the index of the excited atom A). For small R these terms have the form

$$U_n^m(R) = U_+^m(R) - 1/2(n+\Delta(R))^2, \quad R \ll 2n^2, \qquad (33)$$

where Δ is the complex (as a result of the possibility of photoionization) quantum defect, and $U^m_+(R)$ is the ionic term. For R ~ 4 the terms (33) are stabilized. As the atoms separate these states decay, and this can explain the observed Penning peak in the energy spectrum of the ionization electrons[30]

$$A+B \to A_n^*B^m \to A^+ + e + B. \qquad (34)$$

A detailed analysis of the states $A^*_nB^m$ can be carried out in terms of the model of interacting scattering centers proposed previously.[31] Neglecting the negative influence of the electron on direct interaction of the cores, we will write the Hamiltonian of the system in the form

$$\hat{H}(r) = ((-1/2\Delta) - 1/r + u_{eA^+})\hat{1} + \hat{V}_{eB} + \hat{H}_{A^+B}, \qquad (35)$$

where $\hat{1}$ is the unit matrix, $\hat{V}_{eB}$ is the matrix of interaction of the electron with atom B, whose nondiagonal elements are responsible for autoionization at large distances,[32] $\hat{H}_{A^+B}$ is the matrix Hamiltonian of the quasimolecular ion A^+B:

$$H_{11} \equiv (H_{A^+B})_{11} \cong -\beta^0/2R^4, \quad H_{22} \equiv (H_{A^+B})_{22} \approx \omega_B - \beta^m/2R^4 \qquad (36)$$

(β^0 and β^m are the polarizability of atom B in the ground state and the metastable state, $\beta^0 \ll \beta^m$),

$$H_{12} \equiv (H_{A^+B})_{12} \approx C\exp(-\sqrt{-2\epsilon_{A^+}}R) \qquad (37)$$

is the exchange interaction in the system A^+B (ϵ_{A^+} is the ionization potential of the ion).

The interactions u_{eA^+} and u_{eB} depend on the distances to the nucleus of ion A and atom B, respectively, and if their overlap can be neglected, then the problem of finding the eigenvalues of the Hamiltonian (35) reduces to

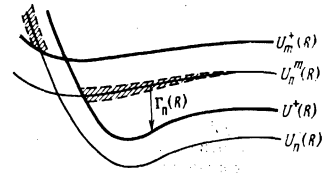

FIG. 3. Terms of the zeroth approximation (in H_{12}) for the quasimolecule AB^m (U^m_n and U_n) and of the ion AB^+ (U^+_m and U^+) with existence of a pseudocrossing in the system of ionic terms. (Only the terms of the n-th state of the Rydberg crowdings are shown.)

solution of a system of algebraic equations containing the physical amplitudes for scattering[21, 31] of the electron by A^+ and B. Taking into account, for example, only s scattering of the electron, we obtain

$$\varkappa_1(R)-G_c^r(E-\omega(R))=\frac{\varkappa_{12}^2(R)}{\varkappa_2(R)-\mathrm{Re}\,G_c^r(E)-i\,\mathrm{Im}\,G_c(E,R)}$$

$$G_c^r(E)=\lim_{R\to R'}[G_c(R,R',E)-1/2\pi|R-R'|], \qquad (38)$$

where $\omega(R)=[(H_{11}-H_{22})^2+4H_{12}^2]^{1/2}$ is the adiabatic splitting of the ionic terms, $\hat{\kappa}_0$ is the matrix of the boundary conditions, which determines the scattering of the slow electron by atom B:[33]

$$\varkappa_1(R)=\varkappa_{11}^0\cos^2\frac{\theta(R)}{2}+\varkappa_{22}^0\sin^2\frac{\theta(R)}{2}+\varkappa_{12}^0\sin\theta(R),$$

$$\varkappa_2(R)=\varkappa_{11}^0\sin^2\frac{\theta(R)}{2}+\varkappa_{22}^0\cos^2\frac{\theta(R)}{2}-\varkappa_{12}^0\sin\theta(R),$$

$$\varkappa_{12}(R)=1/2(\varkappa_{11}^0-\varkappa_{22}^0)\sin\theta(R)+\varkappa_{12}^0\cos\theta(R),$$

$$\mathrm{tg}\,\theta(R)=2H_{12}/(H_{11}-H_{22}), \qquad (39)$$

Analysis of the solutions of Eqs. (38) shows that mainly only terms of states with $l_A \neq 0$ are broadened;

$$\Delta_l(R)=\Delta_l^0(R)-i\delta_l(R). \qquad (40)$$

For $R \gg 1$ we have

$$\Delta_l^0(R)=\pi^{-1}\,\mathrm{arcctg}\,\varkappa_1(R)\sqrt{R/2}, \qquad (41)$$

$$\delta_l(R)=\sin^2(\pi\Delta_L^0)\frac{\varkappa_{12}^2(R)\,\mathrm{Im}\,G_c^{(+)}(\omega-1/2n^2)}{[\varkappa_2(R)-\mathrm{Re}\,G_c^r(\omega-1/2n^2)]^2+[\mathrm{Im}\,G_c^{(+)}(E,R)]^2}. \qquad (42)$$

For fixed R the probability of autoionization is

$$\Gamma_n(R)=\delta(R)/n^3, \qquad (43)$$

i.e., it decreases rapidly with increase of n. However, at the moment of stabilization of the n-th term $\Gamma_n \sim n$ (since $\varkappa_{12} \sim H_{12}(\varkappa_{11}-\varkappa_{22})n^2$), i.e., for $n \sim H_{12}^{-1/2}$ the widths of the levels become of the order of the distances between them. Therefore for small velocities of the nuclei all highly excited states succeed in decaying already at small distances ($R \sim 4$) and the peak of Penning electrons is formed mainly in subsequent decays[29] of the term with n = 1. However, we can expect that for higher energies there will also appear in the differential spectra groups of peaks corresponding to decay of excited Penning states ($n > 1$).

4. Under conditions of accidental resonance of a Penning level with an atomic autoionization level, i.e., in cases where the excitation energy of the metastable atom B^m is close to the excitation energy of one of the inner electrons of atom A ω_A (this occurs, for example, for the pair Hg He^m), a pseudo crossing of these terms is possible (Fig. 4) and the question arises of the probability of nonadiabatic transitions between them. In order to include this possibility in the discussion, it is necessary to separate the additional channel of electron motion in the field of the quasimolecular core in explicit form. For this purpose the system is conveniently described by the two-channel Lippman-Schwinger equation with an optical potential taking into account transitions to states of the elastic channel corresponding to the unexcited quasimolecular ion:

$$\Psi_a=G_aV_{a0}G_0(V_{0a}\Psi_a+V_{0b}\Psi_b),$$

$$\Psi_b=G_bV_{b0}G_0(V_{0a}\Psi_a+V_{0b}\Psi_b). \qquad (44)$$

Here G_S is the Green's function of the outer electron in the field of the ionic core of the s-th configuration (the indices a and b indicate the excitation channel, and the index zero denotes the elastic channel $E = E_0 = E_S + \omega_S$).

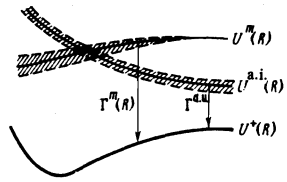

FIG. 4. Pseudocrossing of Penning term $U^m(R)$ with the autoionization term $U^{a.i.}(R)$.

It is assumed that the pseudocrossing occurs at sufficiently large distances permitting us to neglect direct intercore exchange of excitation. The separated nondiagonal interactions of the electron V_{0a} and V_{0b} are responsible for inelastic transitions respectively in systems $A^{a.i.}$ and B^-. In the two-resonance approximation, taking into account only decays and interactions of the states discussed, we have for the energy levels of the system the equation

$$(E-\omega_A-\varepsilon^{a.i.}(R)-\langle\Phi_A^{a.i.}|V_{a0}G_0V_{0a}|\Phi_A^{a.i.}\rangle)(E-\omega_B-\varepsilon_A(R)$$
$$-\langle\Phi|V_{b0}G_0V_{0b}|\Phi\rangle)=\langle\Phi_A^{a.i.}|V_{a0}G_0V_{0b}|\Phi\rangle\langle\Phi|V_{b0}G_0V_{0a}|\Phi_A^{a.i.}\rangle. \qquad (45)$$

Here $\epsilon^{a.i.}(R)$ and $\Phi_A^{a.i.}$ are the binding energy and the wave function of the electron in the autoionization state of atom A interacting with unexcited atom B (without taking into account inelastic transitions); $\epsilon_A(R)$ and Φ are the binding energy and wave function of the electron of atom A in the ground state, calculated with inclusion of the elastic interaction with the metastable atom B^m.

The exchange interaction of the decaying states (the right-hand part in Eq. (45)) depends, as can easily be seen, on the probability of decay of the corresponding noninteracting states, i.e., on the atomic autoionization width $\Gamma^{a.i.}$ and the Penning autoionization width $\Gamma_m(R)$,

$$\Lambda_{ex}^2(R)\sim\Gamma^{a.i.}\Gamma_m(R)/(kR)^2, \quad k^2=2(\omega_A+\varepsilon^{a.i.}). \qquad (46)$$

In the most interesting cases we have $kR \gg 1$ and $\Lambda_{ex}^2 \ll \Gamma^{a.i.}\Gamma_m$, i.e., the exchange interaction of the type discussed, introduced by exchange of an electron, cannot be the cause of nonadiabatic transitions between quasistationary states.

[1)] The probability of autoionization of the quasimolecule in a collision time t_0 is as a rule small ($\Gamma t_0 \sim 0.1$ (ref. 7)), and therefore σ, n(E), and the rate constant of process (1) are proportional [8] to Γ.

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