Inelastic autoionization of quasimolecules and the Penning effect

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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* εB, exceeds the ionization potential of particle A, εA):

\[ A + B^* \rightarrow A^+ + e + B, \]  

(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 $10^{-13}$–$10^{-14}$ 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,$^{[3]}$ photolysis, passage of shock waves, and so forth. A process close to (1)–de-excitation of a mesic atom B$_p$ as the result of ionization of atomic particles–plays an important role in the dynamics of excited states of mesic molecules.$^{[4]}$ 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.$^{[5-7]}$

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 $p$ respectively of the total probability $P(p)$ and differential probability $P(E, p)$ for ionization of the quasimolecule:

\[ \sigma = 2\pi \int P(p) dp, \]  

(2)

\[ n(E) = 2\pi W \int P(E, p) dp. \]  

(3)

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

\[ P(p) = \int_{R_{\min}}^{R_{\max}} P(R, p) dR, \]  

(4)

\[ P(p) = \int_{R_{\min}}^{R_{\max}} P(R, p) dR. \]

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tion of a population inversion of the levels in continuously acting lasers operating in vapors of alkaline earth metals\cite{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 $U^{+}(R)$, $U_{0}^{+}(R)$ (the ground state and n-th excited state of the quasimolecular ion), $U^{0+1+}(R)$ (the term correlating at infinity with autolization of the level of the atom A), and $U^{B0}(R)$ (correlating at infinity with the initial metastable state of the atom B\cite{19}) there is no pseudocrossing, i.e., for all inter-nuclear distances the following condition is satisfied,

$$U^{+}(R)<U^{+}(R)<U^{0+1+}(R),$$

then the main mechanism of process (9) and (10) is inelastic autolization of the quasimolecule, i.e., a vertical electronic transition to levels of the corresponding con- 

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

For the pair H'He, for example, we have the parameter \((\varepsilon_A/\varepsilon_B)\) \(\sim 0.15\). If the conditions (22) are satisfied, it is easy to obtain for the first time (see the similar derivation for the level shift, carried out in ref. 23).

\[ M^{(1)}(k) = \langle F(k) \mid gA \Phi(R) \mid \psi_A^c (R) \rangle. \]  

Here \( R = (R_B - R_A) \) is the radius vector of atom B relative to atom A;

\[ e^s - \int d \vec{r} d \vec{r}' \psi_{B'}(\vec{r}) \psi_{B''}(\vec{r}') \exp[-i \cdot \vec{p} \cdot (\vec{r} - \vec{r}')] \]

is the generalized amplitude for exchange de-excitation of atom Bm by an electron of zero energy \( v = 0 \). In typical cases \( k_0 \gg k_s \), 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 \( \Psi_{2l}(R) \) centered on the nucleus of atom A and taken at the point of location of atom B:

\[ N(\theta, R) = \text{const} \langle F(-i/k, 1, -(kR+kr)) \rangle. \]  

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

For small \( k \) (in the quasiclassical limit)

\[ N(\theta, R) = \text{const} \langle F(\sqrt{i/k, 1, -(kR+kr)}) \rangle. \]  

The observed angular distribution of electrons corresponds to the distribution (25) averaged with a weight \( W(\theta) \) over interatomic distances and impact parameters \( \rho \). 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 \( B_m^1 \) in the vicinity of the turning point, \( R \) (29), and express \( M^{(1)}(k) \) in terms of the physical (experimentally observed) amplitude for breakup of a metastable atom by a slow electron.

The ratio of the inelastic autoionization width \( \Gamma_n \) to the elastic width \( \Gamma_0 \) in this case is equal to the ratio of the cross sections for formation of the excited ion \( A_n^+ \) in the process (29) \( \sigma_n^c \) to the cross section for ionization without excitation \( \sigma_0^c \).

\[ \Gamma_n (k) = \frac{\Gamma_n}{\Gamma_0} \sigma_0^c \sigma_n^c. \]  

The function \( \Gamma_n (k) \) has a maximum in the vicinity of atom B and is exponentially damped at distances of the order of the radius \( R_m^1 \). The interaction \( u_{AB} \) 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) falls off quite rapidly with increasing \( k \).

The main contribution in integration over \( r_1 \) and \( r_2 \) in Eq. (30) is from the two nonoverlapping regions of variation of the variables \( r_1 \) and \( r_2 \). We can assume that \( r_1 > r_2 \) and express \( M^{(1)}(k) \) 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., decreases with increasing velocity of the atoms. Expanding \( \Phi_c \) and \( G_{2l}^1 \) in spherical functions relative to the center of the ion, we find

\[ M^{(1)}(k) = \frac{2\Phi_c^R}{R} \sum_i (2l+1) \chi_{i+1}^{<}(kR) a_{m}(k) P_l(kR) \]  

(Here \( g_0 \) is the amplitude for exchange de-excitation of Bm by a slow electron, \( a_{m}(k) \) is the partial amplitude for inelastic scattering of an electron with energy \( k^2/2 \) by ion \( A^+ \), \( \chi_{i+1}^< \) is the irregular solution of the radial

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Schrödinger equation with a Coulomb potential \( \chi^{(1)} \sim e^{ikr} \).

The angular distribution (asymmetric in the general case) depends on the specific values of \( \alpha_{A}^{(0)}(k) \). The probability of inelastic autoionization and the cross section for inelastic Penning ionization in the ratio \( \sigma_{c}/R^2 \) are less than the cross section for process (1), \( \sigma_{A} \sim \alpha_{A}^{(0)}(\sigma_{A}/v) \). Here \( \sigma_{A}^{(0)} \) is the cross section for excitation of the n-th state of ion \( A' \) by electron impact

\[
e + A' \rightarrow e + A'' \tag{32}
\]

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.\(^{11,12,13,14,15,16,17} \)

The relative yields of various excited states of the ions \( Zn^{+}, Ca^{+}, He^{+} \) in process (29) have been given by Hyman.\(^{28} \)

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 \( n' \), i.e., the quantity \( \omega_{n'} \) and, consequently, the contribution of the first mechanism discussed to the cross section for processes of type (9), has the following values: \( \approx 5\% \) for \( \Delta n = 0, I = 1 \); \( \approx 25\% \) for \( \Delta n = 1, I = 0 \); \( \approx 1\% \) for \( \Delta n = 0, I = 2 \); and \( \approx 0.1\% \) for \( \Delta n = 0, I = 3 \) of the total cross section for process (1) \( \sigma(1) \sim 10^{-15} \text{cm}^2 \) (ref. 1). Typical values of the energy \( \omega_{n'} = eA \) are 10-15 eV. The corresponding cross sections for the processes (30) for ions of divalent atoms have values \( 10^{-15} \text{ cm}^2 \) (ref. 27). For \( R_{0} \sim 5-7 \) atomic units this gives \( \sigma_{c}/R^2 \sim (2-5) \times 10^{-7} \).

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 \( S_{2} \) and \( P_{j} \) 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

\[ Hg^{+} + He \rightarrow Hg^{+}(P_{j}) + e + He \]

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 \( D_{1} \) and \( P_{j} \) ions, the contribution of the second mechanism discussed is dominant. Secondary autoionization 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 \( \approx 3 \times 10^{-17} \text{ cm}^2 \) (\( E \approx 15 \text{ eV} \), the cross section for ionization of \( Ba' \) by electron impact is \( \sigma' \sim 0.7 \times 10^{-15} \text{ cm}^2 \) (ref. 27), \( \sigma(1) \approx 10^{-15} \text{ cm}^2 \).

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, are dominant. In similar cases there is a high probability (\( \approx 100\% \)) for formation of excited ions corresponding to the presence of a "hole" in the d shell.\(^{(11)} \) 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 \( \approx 10^{-17} \text{ cm}^2 \).

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 the energy spectra of excited states of the quasimolecular 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 \( U^{m}(R) \) at infinity correlate with states of a system of the type \( A^{m}B^{m} \) (here \( n \) is the index of the excited atom \( A \)). For small \( R \) these terms have the form

\[ U_{n}^{m}(R) = U_{n}^{m}(R) - 1/2(n+1/2)(n+1/2), \]

where \( A \) is the complex (as a result of the possibility of photoionization) quantum defect, and \( U^{m}(R) \) is the Rydberg term. For \( R \approx 4 \) 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 excitation electrons\(^{(30)} \)

\[ A + B \rightarrow A^{n}B^{m} - A^{n} + e + B. \tag{34} \]

A detailed analysis of the states \( A^{m}B^{m} \) 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

\[ H(r) = H_{Ca} + H_{Sr} + H_{Ba} + \frac{1}{2} \sum_{A+B} U_{n}^{m}(R). \tag{35} \]

where \( n \) is the unit matrix, \( V_{A+B} \) is the matrix of interaction of the electron with atom \( B \), whose nondiagonal elements are responsible for autoionization at large distances,\(^{(32)} \) \( H_{A^{n}B^{m}} \) is the matrix Hamiltonian of the quasimolecular ion \( A' B' \):

\[ H_{A^{n}B^{m}} = (H_{Ca}),_{m}- \beta^{2}/2R^{2}, \]

\[ H_{Sr} = (H_{Sr}),_{m}- \beta^{2}/2R^{2}, \]

\[ H_{Ba} = (H_{Ba}),_{m} = C \exp (-\gamma \sqrt{2\delta_{A}R}). \tag{36} \]

\( \beta^{2} \) and \( \beta^{2} \) are the polarizability of atom \( B \) in the ground state and the metastable state, \( \beta^{2} \leq \beta^{2} \).

\[ H_{A^{n}B^{m}} = (H_{Ca}),_{m}- \beta^{2}/2R^{2}, \tag{37} \]

is the exchange interaction in the system \( A^{n}B^{m} (eA') \) is the ionization potential of the ion).

The interactions \( u_{A^{n}B^{m}} \) and \( u_{A^{n}B^{m}} \) 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 \( H_{3} \)) for the quasimolecular \( A^{m}B^{m} \) (ref. 30) and of the ion \( AB^{m} \) (ref. 30) with existence of a pseudocrossing in the system of ion terms. (Only the terms of the n-th state of the Rydberg crowding are shown.)

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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

\[
x_i(R) - G_i^s(E - \omega(R)) = \frac{x_0^s(R)}{G_i^s(E) - \text{Re} G_i^s(E) - i \text{Im} G_i^s(E, R)}
\]

\[
G_i^s(E) = \lim [G_i(R, R'; E) - 2/n_i(R - R')],
\]

(38)

where \(\omega(R) = \left(\mathbf{H}_i^s - \mathbf{H}_{2s}^l\right)^{1/2}\) is the adiabatic splitting of the ionic terms, \(\sigma_0\) is the matrix of the boundary conditions, which determines the scattering of the slow electron by atom B.[33]

\[
x_i(R) = x_0^s \cos \frac{\theta(R)}{2} + x_n^s \sin \frac{\theta(R)}{2},
\]

(41)

\[
x_i(R) = x_0^s \sin \frac{\theta(R)}{2} + x_n^s \cos \frac{\theta(R)}{2},
\]

(42)

\[
x_i(R) = x_0^s \cos \theta(R) + x_n^s \sin \theta(R),
\]

for fixed R the probability of autoionization is

\[
\Gamma_i(R) = \Delta_i(R) n^i,
\]

(43)

i.e., it decreases rapidly with increase of n, However, at the moment of stabilization of the n-th term the \(\Gamma_n \sim n\) (since \(\kappa_{12} \sim H_{12}^{1/2}\)) 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, 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:

\[
\Psi_i = G_i V_a G_i(V_a \Psi_i + V_m \Psi_m),
\]

\[
\Psi_m = G_m V_a G_i(V_m \Psi_i + V_m \Psi_m).
\]

(44)

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

It is assumed that the pseudocrossing occurs at sufficiently large distances permitting us to neglect direct intercore exchange of excitation. The separated non-diagonal interactions of the electron \(V_{a1}\) and \(V_{b1}\) are responsible for inelastic transitions respectively in systems \(A^{a1}\) and \(B^m\). 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

\[

\begin{align*}
(\mathbf{E} - \omega_a - \epsilon^{a1}(R) - (\mathbf{E} - \omega_b - \epsilon^{b1}(R)) (\mathbf{E} - \omega_a - \omega_s(R))
\end{align*}

=(\Phi^{a1}_{V_a G_i V_m} (\Phi^{b1}_{V_a G_i V_m}) (\mathbf{E} - \omega_a - \omega_s(R))
\]

\[
- (\Phi^{a1}_{V_a G_i V_m} (\Phi^{b1}_{V_a G_i V_m} (\Phi^{a1}_{V_a G_i V_m}) (\mathbf{E} - \omega_a - \omega_s(R))
\]

(45)

Here \(\epsilon^{a1}(R)\) and \(\Phi^{a1}_{V_a G_i V_m}\) 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); \(\epsilon_b(R)\) and \(\Phi^{b1}_{V_a G_i V_m}\) 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 shown, on the probability of decay of the corresponding noninteracting states, i.e., on the atomic autoionization with \(r^{a1}\) and the Penning autoionization width \(\Gamma_{m}^{a1}\).

\[
\Lambda_{in}^{a1} = \Gamma_{m}^{a1} \Gamma_{m}^{b1} (r^{a1} / (kR))^{4}, \quad k^2 = 2\omega_a + \omega_s
\]

(46)

In the most interesting cases we have \(kR \gg 1\) and \(\Lambda_{ex}^{a1} \ll r^{a1} \Gamma_{m}^{b1}\), i.e., the exchange interaction of the type discussed, introduced by exchange of an electron, cannot be the cause of nonadiabatic transitions between quasi-stationary states.

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

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