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PENNING AND STOCHASTIC COLLISIONAL IONIZATION OF ATOMS IN AN EXTERNAL ELECTRIC FIELD

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Abstract. The quantum theory for the Penning and stochastic collisional ionization of atoms in an external electric field is developed and based on the operator perturbation theory and Focker-Plank stochastic equation method. Some estimates of the Penning process cross-sections for He — H, Na pairs are given.

Keywords: Penning ionization, stochastic collisional ionization, external electric field

ПЕННІНГІВСЬКА ТА СТОХАСТИЧНА ІОНІЗАЦІЯ АТОМІВ У ЗОВНІШНЬОМУ ЕЛЕКТРИЧНОМУ ПОЛІ ЗА РАХУНОК ЗІТКНЕНЬ

В. І. Михайленко, Г. О. Кузнецова

Анотація. Розвинуто теорію пеннінгівської та стохастичної іонізації атомів при наявності зовнішнього електричного поля за рахунок зіткнень в межах операторної теорії збурень і методу стохастичного рівняння Фоккер-Планка. Наведені оцінки перерізів пеннінгівського процесу для пар He — H, Na.

Ключові слова: пеннінгівська іонізація, стохастична іонізація за рахунок зіткнень, зовнішнє електричне поле

ПЕННИНГОВСКАЯ И СТОХАСТИЧЕСКАЯ СТОЛКНОВИТЕЛЬНАЯ ИОНИЗАЦИЯ АТОМОВ ВО ВНЕШНЕМ ЭЛЕКТРИЧЕСКОМ ПОЛЕ

В. И. Михайленко, А. А. Кузнецова

Аннотация. Развита квантовая теория пеннинговской и стохастической столкновительной ионизации атомов при наличии внешнего электрического поля на основе формализма операторной теории возмущений и метода стохастического уравнения Фоккера-Планка. Приведены оценки сечений пеннинговского процесса для пар He — H, Na.

Ключевые слова: пеннинговская ионизация, стохастическая столкновительная ионизация, внешнее электрическое поле

1. Introduction

During last several decades a great attention is devoted to the studying elementary atomic processes in plasmas, gases and other mediums [1-21]. The most interesting and simultaneously very complicated phenomena include the ionization of excited atoms by means of the photon and electron impact, atom-atom or ion-atom collisions). Though there are many theoretical and experimental papers, however some important aspects are remained unclear hitherto. It is very difficult to perform an accurate account of the inter electron correlation effects in the electron-atom collisions. These effects and other ones are not adequately described within many simplified models. Situation changes dramatically under consideration of the different atomic collisional processes under availability of the external electromagnetic fields. Even more simple case of the external static electric field is remained hitherto quantitatively undescribed. So, a great interest represents development of the consistent quantum theory of the atomic collisional processes in an external electric field [1-3, 9-14]. One could remind the key interatomic collisional processes, which are of a great interest for plasma science., namely:

$$A^*(nl)+B\rightarrow(A+B^+)+e \text{ or,} \tag{1}$$

$$A^*(nl)+B\rightarrow(A^+ +B)+e \text{ or,} \tag{2}$$

$$A^*(nl)+B\rightarrow AB^+ +e. \tag{3}$$

In these formula A^* denotes the atom in an excited state, B^+ is the ionized atom. The process (3) is corresponding to so called associative ionization. It is well known (look, for example, [1,2]) it takes a place when the dissociation energy of molecular ion AB^+ is more than the ionization potential of the excited atom. The first process (1) takes a place and runs very effectively in a case when the excitation energy of the A atom is more than the ionization potential of the atom B. Here one can introduce the Penning process, which is corresponding to the situation when the atom A is in the metastable state.

The most widespread theoretical schemes for description of the cited processes (look, for example, [1-5,20,21]) are based on the defining the capture cross-section of collisional particles by field of the wan der Waals interaction potential. It should be mentioned several versions of the rectilinear classical trajectories model too [1-3,20]. Similar models, however, do not account for any difference between the Penning process and resonant collisional processes. Moreover, the accuracy of these schemes in many important applications is definitely unsatisfactory especially in a case of little collision energies, whwere trajectories are not surely rectilinear. Naturally, theoretically consistent models should include the data about process probability $G(R)$ as function of the inter nuclear distance. In the last years many author proposed more sophisticated approaches which allow to take into account for many important quantum effects (exchange, correlations etc.). In refs. [15-19] the authors present several new consistent theories for different elementary atomic processes. Though, the the Penning and stochastic collisional ionization of atoms had been a subjecy of intensive theoretical and experimental interest, however, the available level of modelling in not satisfactory [21].

Another important class of tasks problems is connected with an effect of the external electric (electromagnetic field) in a case of the Penning and stochastic collisional ionization, however, hitherto it is absent any adequate quantum theory. Obviously, an external electric (electromagnetic) field could provide a selective governing by cited processes. It explains a great theoretical and applied importance of this problem.

So, the main aim of this work is to present the consistent quantum theory for the Penning and stochastic collisional ionization of atoms in an external electric field. The presented theory is based on the operator perturbation theory [13,14] and Focker-Plank stochastic equation method [17,19].

2. Theory of collisional ionization and operator approach

In order to take into account an external electric field and construct the corresponding electron wave functions one must start for the treating the Stark problem. It is very important to have the zeroth approximation, which includes an external electric field, i.e. the strength of the field is arbitrary. As appropriate theoretical approach for constructing the wave functions in the Stark problem is given by the operator formalism [13,14]. It is important to note that the quantum defect version of this formalism is appropriate for treating alkali atoms and correspondingly the collisional processes with similar atoms. These systems are often represented and a core and a single electron above the N-electron core.

As usually, the Schrodinger equation for atom in an uniform electric field of the nucleus (in atomic units) can be written as follows: :

$$[-(Z-N)/r + \varepsilon z - 0{,}5\Delta - E]\,\psi = 0, \tag{4}$$

where E is the eigen energy, Z — charge of nucleus, N — the number of electrons in atomic core. Within the quantum defect scheme [14,15] of the operator approach [13] it is used the relation between quantum defect value μ_l, electron energy E and principal quantum number n:

$$\mu_l = n - z^*(-2E)^{-1/2}.$$

According to the standard classification, all the electron states in a field are treated due to quantum numbers: n, n_1, n_2, m (principal, parabolic, azimuthal ones). The quantum defect in the parabolic co-ordinates $\delta(n_1 n_2 m)$ is connected with the quantum defect value of the free ($\varepsilon=0$) atom by the following relation [14]:

$$\delta(n_1 n_2 m)=(1/n)\sum_{l=m}^{n-1}(2l+1)(C^{JM}_{J,M-m;lm})^2\mu_l\,,$$

$$J=(n-1)/2,\ M=(n_1-n_2+m)/2.$$

Within the operator scheme [13,14], the separation of variables in Eq. (1) in parabolic co-ordinates results in the system of two equations for the functions f, g:

$$f'' + \frac{|m|+1}{t} f' + [0{,}5E + (\beta_1 - N/Z) / t - 0{,}25\, \varepsilon(t)\, t\,] f = 0, \tag{5a}$$

$$g'' + \frac{|m|+1}{t} g' + [0{,}5E + \beta_2 / t + 0{,}25\, \varepsilon(t)\, t\,] g = 0, \tag{5b}$$

coupled through the constraint on the separation constants: $\beta_1+\beta_2=1$. Within the operator approach the uniform electric field $\varepsilon(t)=\varepsilon_0$ in Eqs. (5) is substituted by some model function $\varepsilon(t)$ with parameter τ ($\tau = 1.5\, t_2$; t_2- is the second turning point). It is important to note that the final results do not depend on the parameter τ . Further it should be reminded that the two turning points for the classical motion along the η axis, t_1 and t_2 , at a given energy E are the solutions of the quadratic equation ($\beta = \beta_1$, $E = E_0$). Within the operator approach [13] one must know the two zeroth order eigen functions of the starting Hamiltonian H_0: bound state function Ψ_{Eb} (ε, ν, φ) and scattering state function Ψ_{Es} (ε, η, φ) with the same eigen energy order to calculate any parameters of the quasi-stationary atomic states. Let us note that the collision process is not accounted here. Definition of the corresponding eigen energies and functions results in the solution of the well known problem of the states quantification in the case of the penetrable barrier. According to ref. [13], the system (5) is solved with the total Hamiltonian H using the conditions, which quantify the bounding energy E, with separation constant β_1 :

$$f(t) \to 0 \text{ at } t \Rightarrow \infty\,,\ \partial x(\beta, E) / \partial E = 0 \tag{6}$$

with

$$x(\beta, E) = \lim_{t\Rightarrow\infty} [\, g^2(t) + \{g'(t) / k\}^2]\, t^{|m|+1}. \tag{7}$$

The further procedure for the 2D eigen value problem results in solving of the system (5) with probe pairs of E, β_1. It is very important [13] that the bound state energy, eigenvalue β_1 and eigen function for the zero order Hamiltonian H_0 coincide with those for the total Hamiltonian H when the field strength at $\varepsilon \to 0$. The scattering states' functions must be orthogonal to the above defined bound state functions and to each other. These functions $g_{E's}$ are defined according to the operator formalism special algorithm [13]. The imaginary part of state energy in the lowest PT order is:

$$Im\, E = G/2 = \pi < \Psi_{Eb}\, |H| \Psi_{Es} >^2 \tag{8}$$

with the general Hamiltonian H (G- resonance width). The state functions Ψ_{Eb} and Ψ_{Es} are assumed to be normalized to unity and by the δ(k -k')-condition, accordingly.

Further one can introduce the definition of complete cross section for collisional process (1) as follows:

$$\sigma = \int_0^\infty 2\pi\rho d\rho \{1 - \exp[-\int_{-\infty}^{+\infty} G(R)dt]\}\,. \tag{9}$$

Here $G(R)$ is a probability of the Auger effect $G(R)= 2\pi|V_{12}|^2 g_2$ (indexes 1and 2 are relating to states: A^*+B and $A+B^++e$; g is a density of the final states; V is operator of interaction between atoms). In a case when ionization process is realized in the repulsive potential of interaction between atoms in the initial channel, the cross-section is:

$$\sigma = (4\pi f_w / v) \int_{R_{tn}}^{\infty} R^2 G(R) \sqrt{1 - U(R) / E}\, dR\,. \tag{10}$$

Here v is the relative velocity of collision, R_{tn} is the minimally possible distance of rapprochement (the turning point); f_w is the probability that the process is permitted on full electron spin of system of the collisional atoms, Further one should have taken into account a possibility of decay in the second and higher orders of perturbation theory on $V(R)$. Such approach may be used as for the Penning ionization description as for ionization through the wan-der-Waalse capture [3,17,18]. In the perturbation theory second and higher orders it is introduced the matrix element:

$$\left\langle 1 \middle| V(R) G_{E_\infty} V(R) ... V(R) \middle| 2 \right\rangle$$

insist of the simple matrix element $\left\langle 1 \middle| V(R) \middle| 2 \right\rangle$ in expression for probability of collisional decay. Here $[1> \equiv [A^*+B>$ is the initial state, $[2> \equiv [A+B^++e>$ is the final state; G_E is the Green function (see below); $E\infty$ is an energy of quasi-molecule A*B under

$R \to \infty$. The latter is corresponding to approximation of the non-interacting atoms.

Naturally it is supposed that the atomic wave functions are constructed within operator approach with external electric field of any strength. Further one can use for operator V(R) the standard expansion on non-reducible tensor operators:

$$V(R)=\sum_{l_1,l_2=1}^{\infty} V_{l_1l_2}(n)\,/\,R^{l_1+l_2+1}\,, \tag{11}$$

$$V_{l_1l_2}(n) = (-1)^{l_2}\sqrt{\frac{(2l_1+2l_2)!}{(2l_1)!(2l_2)!}}(C_{l_1+l_2}(n)\{Q^A_{l_1}\otimes Q^B_{l_2}\}),$$

$$\text{n}=\frac{R}{R}$$

where $\widehat{Q}_{lm}$ is an operator of the 2^l-pole moment of atom and C_{lm} (n) is the modified spherical function. If we suppose that atom A* is in the state with the whole moment J_i and projection on the quantization axe M_i; in the final state the corresponding quantum numbers are $J_f M_f$; The final expression for the full probability of the electron ejection is similar to expressions, obtained in ref. [17,18]:

$$G(R) = \frac{2\pi(2l_1+1)(l_1+1)(2l_1+3)(2l_2+1)(l_2+1)(2l_2+3)}{R^{2l_1+2l_2+8}(2l_i+1)[1+\delta_{l_1l_2}]^2(2J_i+1)}$$

$$\left|\sum_{p_1p_2p_3l_f}(C^{p_1 0}_{l_2+1\,0\,l_1+1\,0})^2\times\right.$$

$$\times(2p_2+1)(2p_3+1)\begin{Bmatrix}1 & l_1 & l_1+1\\ 1 & l_2 & l_2+1\\ p_2 & p_3 & p_1\end{Bmatrix}\left|\sum_{Jl}\begin{Bmatrix}1 & 1 & p_2\\ l_f & l_i & l\end{Bmatrix}\right.$$

$$\left[\begin{Bmatrix}l_2 & l_1 & p_3\\ J_f & J_i & J\end{Bmatrix}\Re^{lf}_{Jl}(l_1,l_2)+\right.$$

$$\left.+(-1)^{l_1+l_2+p_2+p_3}\begin{Bmatrix}l_1 & l_2 & p_3\\ Jf & Ji & J\end{Bmatrix}\Re^{lf}_{Jl}(l_2,l_1)\;\right]^2 . \tag{12}$$

Here the reducible matrix elements are represented as:

$$\Re^{lf}_{J\,l}(l_2,l_1)=$$

$$=\langle n_A J_i; O_B l_i \left\| \widehat{Q}^A_{l_2}\widehat{d}^B g^{A*B_0}_{Jl}\widehat{Q}^A_{l_1}\widehat{d}^B \right\| O_A J_f; El_f\rangle . \tag{13}$$

Here $d^B = Q^B{}_1$ is an operator of the dipole moment of atom B, $g^{A*B0}{}_{Jl}$ is a radial Green function. Because of that the final state of atom $B \mid El_f\rangle$ is a state of continuum with scattering phase δ_{lf} then the fine structure of levels in atom B is not accounted. It is possible to show that the similar expression for G can be received from Eq. (8) within energy approach [10,12].

The attractive perspective for realization the stochastic c collisional process is provided by a case when the atom A in process (1) is highly excited (Rydberg state). The qualitative physical picture is corresponding to a chaotic drift of the Rydberg electron which interacts with the electromagnetic field of dipole (and simultaneously with an external electric field). This interesting physical situation can be adequately treated within generalized theory of chaotic drift for the Coulomb electron in the external microwave field (see refs. [12,15,19]). Then the function of distribution $f(n,t)$ of the Rydberg electron on space of effective quantum numbers n should be introduced. The equation of motion of the Rydberg electron in this case is as follows:

$$\partial f(n,t)/\partial t\, t=\partial/\partial n\,[\Theta(n-N_{min})D®n^3\times$$

$$\times\,\partial f(n,t)/\partial n\,] - \Theta(n-N_{max})G(n,R)f(n,t). \tag{14}$$

Here $\Theta(n-N_{min})$ is the Heviside function. It served here as additive multiplier in the coefficient of diffusion: Dn^3 and provides freeezing of the stochastic processes in region of the low lying states in accordance with the known Cirikov criterion: $N_{min}<n<N_{max}$. For the Rydberg states ($n>N_{max}$) a direct channel of ionization is opened and the electron ejection takes a place. It is important to note that process will be realized with more probability under availability of the external electric field. Naturally, any numerical estimated can be received only on the basis of concrete calculation. It is obvious that the dynamics of the whole process will be very interesting and it is hardly possible to give any exact estimated on the basis of the qualitative conclusions. We may only indicate the estimate for average effective time τ_{dif} for diffusion of electron from level $n=n_0^*$ till the ionization threshold $N_{max}(R_{tn})$ and further into continuum (see refs. [17,19]):

$$\langle\tau_{dif}\rangle(n_0^*)=1/n_0^*-1/N_{max}(R_{tn})+$$

$$+N_{min}(R_{tn})/2N^2_{max}(R_{tn})-N_{min}(R_{tn})/2(n_0^*)^2. \tag{14}$$

The effective collisional time can be found from equality: $\langle\tau_{dif}\rangle(n_0^*)=t_{col}(R_{tn})$, where value of turning point R_{tn} should be preliminary defind. At last, the final expression for constant of ionization K_i (for some temperature T) is standard and given by known formula [3] :

$$K_i = 4\int_0^{\infty} dE_c(E_c^2/T^3)\times$$

$$\times\exp(-2E_c/T)\sqrt{2/\mu}\sqrt{E_c}\,\sigma_i(E_c)\,. \tag{15}$$

3. Some estimates and conclusion

So, above we presented the consistent quantum theory for the Penning and stochastic collisional ionization of atoms in an external electric field, which is in fact based on the combination of the operator perturbation theory formalism for treating the external electric field effect and Focker-Plank stochastic equation method. The last aspects differ the presented theory from the analogous approaches [3, 17-19], where an external electric field is absent. From the other side, despite the obvious consistency of the quantum theory, its practical realization is naturally connected with sufficiently complicated numerical procedure (even accounting availability of such effective numerical codes as "Dirac", "Superatom", Superstructure" and others [4,12,20]). Another sufficiently complicated moment is connected with definition of the diatomic radial matrix elements of the second order. However, here one could use the non-interacting atoms functions anzats when atomic functions are constructed within the operator approach. Besides, there is an algorithm of the two-times summation on the entire set of the collisional atoms states [12,16,17].

In order to demonstrate the important sequences of the theory let us present some qualitative estimates, using the obvious classical particular case of the presented quantum approach, namely, the motion classical rectilinear trajectories approximation [1,3]. As example, we consider the process $He(2^1S_0)+B_0 \rightarrow He(1^1S_0)+B^+_0+e^-$ (B_0=H, Na) under the temperature T=300°K. The Penning process cross-section is given in the classical limit by a simple formula (in atomic units) [1] :

$$\sigma_P = (\frac{9\pi}{11})(\frac{63\pi}{256v})^{2/11}\Gamma(R^2\Gamma)^{2/11}, \qquad (16)$$

where $v=\sqrt{2T/\mu}$ — velocity, μ — normalized mass of collided atoms, R — interatomic distance and Γ is the probability (autoionization width). The experimental values of the cited process cross sections (without external field) are as follows [1,20,21]: σ_P(He-H)=$33\cdot10^{-16}$cm^2 , σ_P(He-Na)=$17\cdot10^{-16}$cm^2. These averaged values indeed define the upper limit of the true values. The known difficulties of the experimental measurement for the Penning cross-section resulted in that the data of different authors are significantly differ, namely, the experimental error reaches ~60% (look [1-3,20,21]). The data, provided by the classical model [18,20], are as follows: σ_P(He-H)=(6-8)$\cdot10^{-16}$cm^2 , σ_P(He-Na)=(7-9)$\cdot10^{-16}$cm^2 for temperature 300°K. The external electric field effect on the Penning process parameters can be different in dependence upon field strength F_0. In particular, if F_0 is not large (<< standard atomic field strength F_A) then the corresponding effect will not be essential. The simple estimates show [9,12] for both processes that in a case of F_0=10^{-3}a.u. the autoionization width is approximately changed in two times. Respectively, the Penning process cross-sections for cited systems will be approximately equal within the classical model as: σ^F_P (He-H)≈$16\cdot10^{-16}$cm^2, σ^F_P (He-Na) ≈$19\cdot10^{-16}$cm^2. Obviously, here speech is about the qualitative estimate as the classical model does not give an adequate quantitative description of the process despite of the consistent quantum approach. Naturally in a case of the strong external field (large strengths F_0~F_A) the direct field ionization channel may become dominant. In a case of the stochastic collisional process, in particular, with Rydberg collided atoms, the external filed effect can essentially destroy the stochastic mechanism, providing relatively quick field ionization [9,12]. The known phenomenal effect is the effect giant broadening the Rydberg thulium and gadolinium lanthanide atoms autoionization resonances widths in a weak (~100V/cm) field, described in refs. [12,13]. So, an availability of external field can lead to significant changing of the collisional parameters in dependence upon the field strength and, generally speaking, make more complicated the physics of the cited processes. Moreover, it should be noted that the cited processes take a place in the plasma (gas) mediums [1]. Obviously, here, as a rule, it is necessary to make averaging of the characteristics on the Maxwell distribution of atoms. Besides, an external electric field for separated atom should be self-consistently defined and the collective effects should be taken into account for an interatomic interaction potential (for example, within Debae shielding approach [22,23]) in a plasma, the mutual cross-effect of stochastic ionization and distribution of Rydberg atoms etc. At last, let us note that the presented approach can be used for studying not only the Penning ionization processes, but also for defining probabilities of other collisional processes, which are of a great importance for different applications, including, the construction of the plasma chemical sensors, gas discharge devices etc.

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