CLASSICAL APPROXIMATION IN THE THEORY OF INELASTIC COLLISIONS OF HIGHLY EXCITED ATOMS WITH CHARGED PARTICLES

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The problem of calculating the effective cross sections for inelastic collisions between highly excited atoms and electrons can be reduced in the quasiclassical approximation to the determination of the action-function increment in the collisions, i.e., to integration of the classical Hamilton-Jacobi equation. This approach removes the known difficulties connected with the determination of cross sections by the classical method and enables one to obtain these cross sections as a limiting case, an alternative to perturbation theory. An interpolation formula is proposed for the general case. The nature of the approximation is illustrated in the case of the dipole approximation.

1 Approximate methods of calculating effective cross sections of inelastic collisions of atoms with charged particles, based on classical mechanics (see, for example,[1-4])[1], have recently become widespread. The interest in such a method results mainly from the possibility of taking into account more naturally perturbation effects of the motion of the atomic electrons during the collisions. This effect plays a primary role in inelastic collisions; however, allowance for it within the ordinary approximations of quantum mechanical methods is extremely difficult.

In concrete calculations within the classical method, the effective transition cross section is usually defined in the following manner:

$$\sigma = \int_{\varepsilon_1}^{\varepsilon_2} \frac{d\sigma}{d\varepsilon} d\varepsilon, \tag{1}$$

where $d\sigma/d\epsilon$ is the differential cross section of energy transfer from the incident particle to the atom, ϵ_1 is the energy threshold of the reaction channel under consideration, and ϵ_2 is the energy threshold of the following channel. The various approximate methods differ in the means of calculating ϵ as a function of the collision parameters and of averaging $d\sigma/d\epsilon$ over those parameters.

However, such methods of determining the transition cross section (1) include an essential element of arbitrariness. The difficulties in the determination of transition cross sections between stationary states from the classical energy transfer cross section $d\sigma/d\epsilon$ are due to the fact that a trajectory description of the motion of an atomic electron is used in calculating $d\sigma/d\epsilon$. At the same time it is well known that there is no transition into a trajectory motion on going to the limit of the classical stationary state.

It is therefore more consistent to consider the whole set of classical trajectories and to formulate the problem of the classical calculation as the problem of evaluating the action-function increment during collisions. As shown below, such an approach enables one to retain the quantum mechanical definition of a cross section, using classical mechanics only to approximate the quantities appearing in it. It also becomes possible to establish applicability conditions for equations like (1) and to obtain a fuller expression when those conditions are not fulfilled.

In what follows we will have in mind transitions between levels with large values of the principal quantum number n. It is exactly for these states that classical methods are most naturally applicable.

2. We start from the quasiclassical approximation for atomic wave functions $\Psi_n = \exp(iS_n/\hbar)$. The $n \to n'$ transition probability equals

$$W_{n'n} = \lim_{t\to\infty} |\langle \Psi_{n'}^{0}(t) | \Psi_n(t) \rangle|^2 = \lim_{t\to\infty} \left| \left\langle \exp\left(\frac{i}{\hbar} S_{n'}^{0}\right) \right| \exp\left(\frac{i}{\hbar} S_n\right) \right\rangle \right|^2 . \tag{2}$$

Here the index 0 corresponds to the unperturbed atom, and $\Psi_n(t) \to \Psi_n^0$ when $t \to -\infty$. In the quasiclassical approximation S is the action function, determined by the Hamilton-Jacobi equations and by the initial conditions $S_n(-\infty) = S_n^0$. The unperturbed quantities S_n^0 obey the Bohr quantization rules.

In case of a discrete spectrum it is convenient to express the function S in terms of canonical variables for the isolated atom, the action I, and the conjugate phase variable w. In these variables the Hamilton equations for the isolated atom, the action function S^0, and the quantization condition are of the form (see, for example,[5])

$$\frac{\partial H_0}{\partial w} = 0, \quad \frac{\partial H_0}{\partial I} = \frac{\omega}{2\pi} \quad S^0 = Iw - E_n t, \quad I = 2\pi n\hbar, \tag{3}$$

where $\omega = \omega(n)$ is the classical frequency of motion of an electron in an orbit of energy $E = E_n$[2].

For the transition probability $n \to n'$ we have

$$W_{n'n} = \lim_{t\to\infty} \left| \int_0^t dw \exp\left[-2\pi i k w + \frac{i}{\hbar} S'(w, t) \right] \right|^2 . \tag{4}$$

Here $S' = S_n - S_n^0$ is the action increment as the result of the perturbation, and $k = n - n'$. In what follows we use the notation $S'(w, \infty) \equiv S'(w)$. It is easy to verify that (4) satisfies the normalization condition. Since in the interval $0 < w < 1$

[1] Detailed references are contained in [4].

[2] For simplicity we confine ourselves to one pair of variables I and w, corresponding to the principal quantum number n.

$$\sum_k e^{2\pi i k(w-w')} = \delta(w-w'),$$

we have

$$\sum_{n'} W_{n'n} = \int_0^1 \int_0^1 dw\, dw' \delta(w-w') \exp\left\{\frac{i}{\hbar}[S'(w)-S'(w')]\right\} = 1. \quad (5)$$

The transition probability between stationary states of the atom is determined, by Eqs. (2) and (4), in terms of the classical action function S. This function, and consequently also its increment due to the perturbation S′, are found by integrating the Hamilton-Jacobi equation.

3. Consider first the case of a sufficiently strong interaction, when S′ is large compared with ħ. We assume also that the function S′/ħ satisfies the well known conditions, permitting the use of the steepest-descent method in calculating (4). Then

$$\int_0^1 dw \exp\left[-2\pi i k w + \frac{i}{\hbar} S'(w)\right]$$
$$\approx \sum_j \exp\left\{i\left[-2\pi k w_j + \frac{S'(w_j)}{\hbar} + \frac{\pi}{4}\right]\right\} \cdot \left|\frac{1}{2\pi\hbar}\frac{\partial^2 S'}{\partial w^2}\right|^{-1/2}_{w=w_j}. \quad (6)$$

The summation is over the points of stationary phase w_j, determined by the equation $\partial S'/\partial w = 2\pi\hbar k$. Since $S'/\hbar \gg 1$, interference terms can be neglected in calculating the square of the absolute value of Eq. (6)[3]. Hence

$$W_{n'n} = 2\pi\hbar \sum_j \left|\frac{\partial\Delta}{\partial w}\right|^{-1}_{\Delta=2\pi\hbar k}, \quad \Delta = \frac{\partial S'}{\partial w} = I - 2\pi n\hbar. \quad (7)$$

The transition probability is determined by Eq. (7) as a function of the collision parameters, particularly the impact parameter ρ. We therefore have for the transition cross section $\sigma_{n'n}$

$$\sigma_{n'n} = 2\pi \int_0^\infty W_{n'n}(\rho)\rho d\rho = 4\pi^2\hbar \int_0^\infty \left|\frac{\partial\Delta}{\partial w}\right|^{-1}_{\Delta=2\pi\hbar k} \rho d\rho. \quad (8)$$

It is easy to show that this equation is similar in structure to Eq. (1). We proceed to integrate (8) over w. Taking into account, that the variables ρ and w are connected by the equation $\Delta(\rho, w) = 2\pi\hbar k$, we obtain

$$\sigma_{n'n} = 4\pi^2\hbar \int dw \rho(\Delta, w) \left|\frac{d\rho(\Delta, w)}{d\Delta}\right|_{\Delta=2\pi\hbar k}. \quad (9)$$

Introducing the notation $\epsilon = E - E_n$ and using (3) and (7), we have

$$\left|\frac{d\rho}{d\Delta}\right|_{\Delta=2\pi\hbar k} = \frac{d\rho}{dE}\frac{dE}{dI}\Big|_{E=E_{n'}} = \frac{\omega(n')}{2\pi}\left|\frac{d\rho}{d\varepsilon}\right|_{\varepsilon=E_{n'}-E_n}.$$

Since

$$\int dw\, 2\pi\rho \left|\frac{d\rho}{d\varepsilon}\right| = \frac{d\sigma}{d\varepsilon},$$

where $d\sigma/d\epsilon$ is the classical differential cross section for energy transfer, averaged over the "initial phase" w, we obtain from (9)

$$\sigma_{n'n} = \hbar\omega(n')\left(\frac{d\sigma}{d\varepsilon}\right)_{\varepsilon=E_{n'}-E_n}, \quad (10)$$

where $\omega(n')$ is the classical frequency of motion with energy $E_{n'}$, and $\hbar\omega(n') \approx E_{n'} - E_{n'-1} \approx E_{n'+1} - E_{n'}$. The classical equation (1) follows from (10) by the theorem of the mean after a proper choice of the limits ϵ_1 and ϵ_2. The usual prescription for choosing ϵ_1 and ϵ_2 in Eq. (1) secures the correct value of the difference $\epsilon_2 - \epsilon_1 = \hbar\omega(n')$, but leads to somewhat different values of the cross sections $\sigma_{n'n}$. The maximum difference occurs for k = 1.

If (10) is summed over the group of levels n′ contained in a finite energy interval ΔE, and the result obtained is extended to the continuous spectrum, we obtain the ionization cross section. The result coincides with the expression for the ionization cross section obtained from (1) (for $\epsilon_1 = E_n$ and $\epsilon_2 = \infty$).

It follows from the given conclusions that Eqs. (1) and (10) are valid only if the following conditions are satisfied:

1) The equation $\partial S'/\partial w = 2\pi\hbar k$ must be satisfied at least at one point w_j in the interval $0 < w < 1$.

2) At the points w_j the inequality $|\partial^2 S'/\partial w^2|_{w_j} \gg \hbar$ must hold.

Since S′ is such a function of the impact parameter ρ that $S' \to 0$ as $\rho \to \infty$, it is evident that Eqs. (1) and (10) describe the contribution of collisions with sufficiently small ρ to the cross section, and by no means the total cross sections.

4. We turn now to consider the other limiting case of small S′, when perturbation theory can be used. We note that in this case two stages are involved in passing to perturbation theory: when $S' \ll S^0$ classical perturbation theory can be used, and when the stronger condition $S' \ll \hbar$ is satisfied additional simplifications are reached, following which the nature of the approximation becomes similar to quantum perturbation theory.

When $S' \ll S^0$ we have from the Hamilton-Jacobi equation for S the following equation for S′[5]:

$$\frac{\partial S'}{\partial t} - \frac{\omega(n)}{2\pi}\frac{\partial S'}{\partial w} = V\left(w, t, \frac{\partial S_0}{\partial w}\right), \quad (11)$$
$$S'(w, t \to -\infty) = 0,$$

where V is the interaction of the atomic electron with the perturbing particle. We expand V in a Fourier series in w and look for S′ in the form

$$S'(w,t) = \sum_m a_m(t) e^{im(2\pi w + \omega t)}. \quad (12)$$

Then

$$a_m(t) = \int_{-\infty}^t V_m(t') e^{-im\omega t'} dt', \quad (13)$$
$$V_m(t) = \int_0^1 V\left(w, t, \frac{\partial S^0}{\partial w}\right) e^{-2\pi i m w} dw.$$

At the same time

$$W_{n'n} = \left|\int_0^1 dw \exp\left[-2\pi i k w + \frac{i}{\hbar}\sum_m a_m e^{2\pi i m w}\right]\right|^2, \quad (14)$$
$$a_m \equiv a_m(\infty).$$

When $S' \ll \hbar$ this equation is considerably simplified. Expanding the exponential in a series and retaining the first non-vanishing terms, we obtain for $k \neq 0$, the case of interest to us,

$$W_{n'n} = \left|\frac{i}{\hbar} a_n\right|^2 = \frac{1}{\hbar^2}\left|\int_{-\infty}^{\infty} V_k(t) e^{ik\omega t} dt\right|^2. \quad (15)$$

It is well known that as $n \to \infty$ the matrix element

[3] We note that in the collision problems of interest to us there is usually one stationary point.

$V_{n+k,n}$ changes into the Fourier component V_k. Consequently, Eq. (15) coincides with the quantum expression for $W_{n'n}$ in the first approximation of perturbation theory.

Since the applicability condition of (15) $S' \ll \hbar$ is an alternative to the applicability condition of (10) $S' \gg \hbar$, we can use for the total cross section $\sigma_{n'n}$ the approximate expression[4)]

$$\sigma_{n'n} = \sigma_{n'n}^{cl} + 2\pi \int_{\rho_0}^{\infty} \left| \frac{a_k}{\hbar} \right|^2 \rho d\rho, \tag{16}$$

$$\sigma_{n'n}^{cl} = \hbar\omega(n') \left(\frac{d\sigma}{d\varepsilon} \right)_{\varepsilon = E_{n'} - E_n}, \tag{16a}$$

$$S'_{max}(\rho_0) - S'_{min}(\rho_0) = \hbar. \tag{16b}$$

The quantities S'_{max} and S'_{min} in Eq. (16b), which determines ρ_0, are the largest and smallest values of S' in the interval $0 < w < 1$. The second term in (16) gives the correction to the contribution of the region of large ρ, not taken account of in (1) and (10). As will be seen later, in several cases this term may become dominant.

From the applicability condition of (10) it follows that the first term in (11) describes the region $\rho < \rho_k$, where ρ_k is the maximum value of ρ for which the equation $\partial S'/\partial w = 2\pi\hbar k$ has a solution. As a rule $\rho_k < \rho_0$. For this reason the contribution of the region $\rho_k < \rho < \rho_0$ was not taken into account in Eq. (16). We return to this problem below, when we consider the dipole potential.

Concluding this section we note that for highly excited levels $n \gg 1$ the applicability region of the classical perturbation-theory equation (14) $S' \ll S^0 \approx n\hbar$ is much wider than the applicability region of (15) and can, therefore, significantly overlap also the applicability regions of (1), (10), and (16). One can therefore expect good results when calculating σ by numerical integration of Eq. (11).

5. We consider now the concrete example of a dipole interaction, in which case it is possible to perform the calculation analytically. Let the perturbing particle of charge e' move in a straight-line trajectory with velocity v. In the approximation of the rotating quantization axis (the z-axis being directed at the perturbing particle) we have

$$V = |ee'| \frac{z(w)}{\rho^2 + v^2t^2}, \tag{17}$$

where z(w) is the component of the radius-vector of an atomic electron. Using the well known parametric dependence of z on w, expanding z(w) in a Fourier series in w and limiting ourselves to the Kramers approximation (see[5]), it is easy to obtain

$$V_m(t) = \frac{|e'e| a_0 n^2}{3^{1/4}\pi^{1/2} Z_i m^2 (\rho^2 + v^2t^2)}, \quad m \ll n, \tag{18}$$

where $Z_i e$ is the charge of the atomic core (for a neutral atom $Z_i = 1$). From (13) and (12) we also find[5)]

$$a_m = \frac{\pi\alpha}{m^2\rho v} e^{-m\omega\rho/v}, \quad \alpha = \frac{|e'e| a_0 n^2}{3^{1/4}\pi^{1/2} Z_i}, \tag{19}$$

$$S' = \int_0^w dw \frac{2\pi^2\alpha i}{\rho v} \ln \frac{1 - \exp(-\omega\rho/v - 2\pi i w)}{1 - \exp(-\omega\rho/v + 2\pi i w)}. \tag{20}$$

Here and below the argument n of $\omega(n)$ is omitted.

When $\rho > 2\pi^2\alpha/\hbar v$ the inequality $S' \ll h$ holds, which allows the use of perturbation theory. We then have

$$W_{n'n} = \left(\frac{\pi\alpha}{\hbar v \rho k^2} \right)^2 e^{-2k\omega\rho/v}, \quad \rho < \rho_0 = \frac{2\pi^2\alpha}{\hbar v}. \tag{21}$$

For sufficiently small ρ, when $e^{-\omega\rho/v}$ in (20) can be replaced by unity,

$$S' = \frac{2\pi^3\alpha}{v\rho} (w + w^2), \tag{22}$$

$$W_{n'n} = \frac{\hbar v \rho}{4\pi^2\alpha} \{ [C(x_+) - C(x_-)]^2 + [S(x_+) - S(x_-)]^2 \}, \tag{23}$$

where C and S are the Fresnel integrals[6], and

$$x_\pm = \sqrt{\frac{\pi k}{2}} \left(\sqrt{\frac{\hbar v \rho k}{\pi^2\alpha}} \pm \sqrt{\frac{\pi^2\alpha}{\hbar v \rho k}} \right). \tag{24}$$

Equations (22) and (23) are valid in the region $\rho < v/\omega k$. The condition $\rho < v/\omega$ is insufficient, since according to (4) the transition probability is determined by the k-th Fourier component of the quantity $e^{iS'/\hbar}$ and, therefore, the approximate equality of the first k Fourier components of S' in (20) and (22) is required.

If $\rho_0 < v/\omega k$ the applicability regions of (21) and (23) overlap[6)]. For this the condition $2\pi^2\alpha\omega k/\hbar v^2 < 1$ must be satisfied. In the case of excitations by electrons this condition may be written down in the form $10k\ Ry/nE < 1$, where Ry = 13.6 ev and E is the electron energy. In the case of interest to us, $n \gg 1$ and $k \ll n$, this condition is practically always satisfied.

Thus,

$$\sigma_{n'n} = 2\pi \int_0^{\rho_0} W'(\rho) \rho d\rho + 2\pi \int_{\rho_0}^{\infty} W''(\rho) \rho d\rho, \tag{25}$$

where the transition probabilities W' and W'' are determined by Eqs. (23) and (21), respectively.

We turn now to the approximate equation (16). We recall that its first term $\sigma_{n'n}^{cl}$ corresponds to the ordinarily used classical approximation for the cross section. The nature of this approximation can be illustrated with the dipole potential as an example. Using (7), (8), and (22), it is not difficult to obtain

$$W_{n'n}(\rho) = \begin{cases} \rho/2k\rho_k^2, & \rho \leqslant \rho_k, \\ 0, & \rho > \rho_k, \end{cases} \tag{26}$$

$$\rho_k = \pi^2\alpha/\hbar v k, \quad \sigma_{n'n} = \pi\rho_k^2/3k. \tag{27}$$

For sufficiently small ρ Eqs. (26) and (23) coincide. At the point $\rho = \rho_k$, however, (26) gives an overestimate by a factor of four, since $W'(\rho_k) = (8k)^{-1}$. Thus, the contribution of the region $\rho \leq \rho_k$ to σ^{cl} is overestimated, while the contribution of the region $\rho > \rho_k$ is generally disregarded.

It is natural to separate from the region $\rho > \rho_k$ the applicability region of perturbation theory, $\rho > \rho_0$, the contribution of which is determined by the second term

4) For simplicity we write down from here on the inequality for S' instead of $S'_{max} = S'_{min}$ (see (16b)). We note that in the example considered below $S'_{min} = 0$ (see (20)).

5) In obtaining (20), the summation over m was extended to infinity. This imposes the additional condition $\rho > v\omega/n$, which is not important for what follows.

6) It is not difficult to verify that in the range $\rho_0 < \rho < v/\omega k$ Eqs. (21) and (23) give practically the same result.

in (25). The contribution of the intermediate region $\rho_k < \rho < \rho_0$ is estimated below. It is easy to show that in this region $W(\rho) \gtrsim W''(\rho)$. Taking this into account, the total cross section (25) can be approximately calculated, using (26) for $0 < \rho < \rho_k$ and W'' for $\rho > \rho_k$. We finally obtain

$$\sigma_{n'n} = \frac{\pi^5}{3k^3}\left(\frac{\alpha}{\hbar v}\right)^2\left[1 + \frac{6}{\pi^2 k}\ln\frac{\hbar v^2}{2\pi^2\gamma\omega\alpha}\right], \qquad (28)$$

where $\gamma = 1.78$.

It is interesting to compare this equation with the result of calculating σ^{cl} for an excitation by an electron in the impulse approximation (see, for example,[1,2]). From the discussion in[1,2] it follows that

$$\sigma_{n'n} \simeq \frac{4\pi}{3k^3}\frac{a_0^2 n^4}{Z_i^2}\left(\frac{e^2}{\hbar v}\right)^2. \qquad (29)$$

This expression differs from $\sigma^{cl}_{n'n}$ in the dipole approximation (the first term in (28)) by the numerical factor $\pi^3/12\sqrt{3}$, but gives an identical dependence of the results on the parameters. This justifies the assumption that the ratio of both terms in the square brackets in (28) describes in fact the relative role of collisions with small ($\rho < \rho_k$) and large ($\rho > \rho_k$) impact parameters. The latter is particularly important for transitions to adjacent levels and for not too small velocities may give the main contribution to the cross section.

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