Collisions accompanied by excitation transfer between atoms with large angular momenta

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The excitation-transfer cross section is calculated for collisions between excited and unexcited atoms possessing a small resonance effect. It is assumed that the excited and ground states of each of the atoms are coupled by an allowed dipole transition and the angular momenta of these stages are large. It is demonstrated that at a small resonance defect the excitation transfer cross section exceeds the corresponding resonant cross section.

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To investigate various physical processes that occur in gas systems with participation of excited atoms, it is necessary to know the effective cross sections for collisions with excitation transfer. These cross sections were calculated, e.g., in[1-6] for resonant collisions, i.e., collisions of like atoms, excited and unexcited.

We consider in this paper collisions with excitation transfer in the presence of a small resonance defect Δ. Collisions of this kind determine, in particular, the course of definite selective chemical reactions in gas mixtures. These include, e.g., reactions with excitation transfer in collisions of atoms of different isotopes of the same element.

We consider collisions of atoms having large proper angular momenta j_1 and j_2 of the ground and excited states, $j_1 \gg 1$ and $j_2 \gg 1$. This condition is satisfied by a number of elements in the middle and end of the periodic table. For example, for iron and nickel we have $j = 4$, for uranium $j = 6$, etc. The condition $j_1 \gg 1$ and $j_2 \gg 1$ makes it possible to obtain an analytic solution at a resonance defect that is small in comparison with the reciprocal effective collision time, or, equivalently, in comparison with the energy of the interaction of the atoms at the effective distances.

We assume that the excited and ground state of each of the colliding atoms are coupled by an allowed dipole transition. Then the interaction of the atoms is described by the dipole-dipole interaction operator. The resonant collisions of the excited and unexcited atoms are characterized by distances on the order of the Weisskopf radius[7] $\rho_0 \sim d/\sqrt{v}$, where v is the relative velocity of the atoms (we are using the atomic system of units with $\hbar = m = e = 1$).

In the impact-parameter approximation (see, e.g.,[1-6]), we obtain the equations for the amplitudes $\psi_{1\alpha\beta_0}$ and $\psi_{2\alpha_0\beta}$, which describe the possible states of a system of two colliding atoms. The amplitude $\psi_{1\alpha\beta_0}$ corresponds to the case when the first atom is in an excited state α, and the second in the ground state β_0, while the amplitude $\psi_{2\alpha_0\beta}$ corresponds to the case when, to the contrary, the first atom is in the ground state α_0 and the second in the excited state β. The equations take the form

$$i\frac{\partial\psi_{1\alpha\beta_0}}{\partial t}=\langle\alpha\beta_0|\hat V|\alpha_0'\beta'\rangle e^{i\Delta t}\psi_{2\alpha'_0\beta'},$$
$$i\frac{\partial\psi_{2\alpha_0\beta}}{\partial t}=\langle\alpha_0\beta|\hat V|\alpha'\beta'_0\rangle e^{-i\Delta t}\psi_{1\alpha'\beta_0'}, \tag{1}$$

where Δ denotes the resonance defect

$$\Delta=E_\alpha+E_{\beta_0}-E_{\alpha_0}-E_\beta,$$
$$\hat V=[R^2\hat{\mathbf d}_1\hat{\mathbf d}_2-3(\hat{\mathbf d}_1\mathbf R)(\hat{\mathbf d}_2\mathbf R)]/R^5, \tag{2}$$

$\hat{\mathbf d}_1 \equiv \mathbf d_{1\alpha\alpha}$ and $\hat{\mathbf d}_2 \equiv \mathbf d_{\beta\beta_0}$ are the operators of the dipole moments of the atoms, R is the distance between the colliding atoms, $R^2 = v^2t^2 + \rho^2$, and ρ is the impact parameter. Collisions with excitation transfer were investigated in[8-11], where the model Hamiltonian $V \sim CR^{-3}$ was used instead of (2). The probability of the transitions to states of other energy is neglected in (1). This is correct if the closely-lying energy levels of each of the atoms are separated from the given excited state by an energy interval exceeding the energy of interaction over the effective distance $\rho \sim \rho_0$.

If the angular momenta of the excited and ground states of each of the atoms are equal, then the matrices $\hat V$ in Eqs. (1) coincide. We shall considere here just this case, although the final results do not depend on this assumption in the approximation under consideration.

Assume that the first atom was excited prior to the collision. Then collision with excitation transfer is described by the amplitude ψ_2. We express the amplitudes ψ_1 and ψ_2 in terms of the operator $\hat S$:

$$\begin{pmatrix}\psi_1(t,\rho)\\ \psi_2(t,\rho)\end{pmatrix}=\hat S(t,\rho)\begin{pmatrix}\psi_1(-\infty,\rho)\\ \psi_2(-\infty,\rho)\end{pmatrix}, \tag{3}$$

which satisfies according to (1) the equation

$$i\frac{\partial\hat S}{\partial t}=\hat V(\sigma_x\cos\Delta t-\sigma_y\sin\Delta t)\hat S \tag{4}$$

with initial condition

$$\hat S(-\infty,\rho)=1. \tag{5}$$

σ_x and σ_y in (4) denote the Pauli matrices acting in the space (ψ_1, ψ_2). We solve Eq. (4) in the quasiclassical approximation. We base ourselves on the condition that the proper angular momenta j_1 and j_2 of the colliding atoms are large, i.e., both the ground and the excited state of each of the colliding atoms correspond to a large number $(2j_1 + 1)$ and $(2j_2 + 1)$ of eigenfunctions. The dipole-moment operators $\hat{\mathbf d}_1$ and $\hat{\mathbf d}_2$ of the colliding atoms can then be replaced by classical vectors $\mathbf d_1$ and $\mathbf d_2$ whose lengths are determined by the reduced matrix elements of the operators $\hat{\mathbf d}_1$ and $\hat{\mathbf d}_2$ taken between the corresponding atomc states:

$$\hat{\mathbf d}_i\to\mathbf d_i=\mathbf n_i d_i/\sqrt{2j_i},\quad i=1,2, \tag{6}$$

where $\mathbf n_i$ are unit vectors and d_i are the moduli of the reduced matrix elements of the dipole-moment operators, taken between the considered atomic states (see, e.g.,[12]).

The excitation-transfer cross section is expressed in terms of the element $S_{21}(\infty, \rho)$ of the matrix $S(\infty, \rho)$

$$\sigma=\int_0^\infty 2\pi\rho\langle|S_{21}(\infty,\rho)|^2\rangle d\rho, \tag{7}$$

where the angle brackets denote averaging over the directions of the vectors d_1 and d_2. This averaging over the directions corresponds to summation and averaging over the polarizations of the final and initial atomic states in the consistent quantum approach.

We seek the matrix S in the form

$$S=S_0S_1, \tag{8}$$

where the matrix $S_0(t, \rho)$ describes collisions with resonant excitation transfer. It satisfies Eq. (4) at $\Delta = 0$:

$$S_0(t,\rho)=\exp\left(-i\sigma_x\int_{-\infty}^t V\,dt\right). \tag{9}$$

The solution (9) is valid when the operators $\hat{d}_1$ and $\hat{d}_2$ are replaced by the classical vectors d_1 and d_2. All the commutators of the type $[V(t_1), V(t_2)]$ then vanish. This means, however, not only neglect of the quantum correction, but also the assumption that the classical vectors d_1 and d_2 can be regarded as invariant, i.e., their angle of rotation during the collision process is small. It can be shown that this corresponds to neglecting the terms of order j^{-1} in comparison with unity. Thus, our results are valid accurate to terms of order j^{-1} ($j \sim j_1 \sim j_2$).

The matrix S_1, as follows from (4), (8), and (9), satisfies the equation

$$i\frac{\partial S_1}{\partial t}=US_1, \quad S_1(-\infty,\rho)=1, \tag{10}$$

and the matrix U is given by

$$U=S_0^{-1}\{V[\sigma_x(\cos\Delta t-1)-\sigma_y\sin\Delta t]\}S_0=V[\sigma_x(\cos\Delta t-1)$$
$$-\sigma_y\sin\Delta t\cos 2\varphi(t)+\sigma_z\sin\Delta t\sin 2\varphi(t)], \quad \varphi(t)=\int_{-\infty}^t V\,dt.$$

Assuming the resonance defect Δ to be small, we solve (10) by perturbation theory accurate to terms quadratic in Δ. We obtain accordingly

$$|S_{21}(\infty,\rho)|^2=\sin^2\alpha-(A_1+A_2)\sin 2\alpha$$
$$+B^2\cos^2\alpha+C^2\sin^2\alpha+BC\sin 2\alpha-2D\sin^2\alpha, \tag{11}$$

where

$$\alpha=\varphi(\infty)=-\frac{d_1d_2}{\sqrt{j_1j_2}}\frac{1}{\rho^2 v}\xi, \quad \xi=n_{1x}n_{2x}-n_{1z}n_{2z},$$

$$A_1=\int_{-\infty}^{\infty}V(1-\cos\Delta t)\,dt, \quad B=\int_{-\infty}^{\infty}V\sin\Delta t\cos 2\varphi(t)\,dt, \tag{12}$$

$$D=\int_{-\infty}^{\infty}dt_1\int_{-\infty}^{t_1}dt_2V(t_1)V(t_2)\sin\Delta t_1\sin\Delta t_2\cos 2[\varphi(t_2)-\varphi(t_1)].$$

The expressions for C and A_2 are obtained respectively from the expressions for B and D by replacing the last cosine by a sine.

We substitute (11) in (7) and integrate with respect to the impact parameter ρ. Retaining the terms that do not vanish after averaging over the directions of the vectors n_1 and n_2, we get

$$\sigma=\frac{\pi^2 d_1d_2}{2(j_1j_2)^{1/2}\hbar v}\left\{\langle|\xi|\rangle-\frac{\lambda^2}{2\pi}\left[\left\langle\xi^2\left(\ln\frac{4}{\gamma^3\lambda^2|\xi|}+2\right)\right\rangle\right.\right.$$
$$\left.\left.-2\langle\eta^2\rangle\left(\ln\frac{8}{\gamma^3\lambda^2}-1\right)+L\right]\right\}, \tag{13}$$

where the angle brackets again denote averaging over the directions of the vectors n_1 and n_2:

$$\eta=n_{1x}n_{2y}+n_{1y}n_{2x},$$

$\ln\gamma = C$ is the Euler constant, and λ is a dimensionless small parameter equal to the ratio of the resonance defect Δ to the interaction at distances on the order of the Weisskopf radius ρ_0,

$$\lambda^2=\frac{2d_1d_2\Delta}{(j_1j_2)^{1/2}(\hbar v)^3}.$$

All the calculations were made accurate to terms of order λ^2.

By L we denote the expression

$$L=\frac{1}{2}\int_{-\infty}^{\infty}d\tau_1\int_{-\infty}^{\tau_1}d\tau_2\,\tau_1\tau_2\left\langle h(\tau_1)h(\tau_2)\ln\left|\left(\int_{-\infty}^{\tau_1}h(\tau)d\tau\right)^2-\left(\int_{\tau_1}^{\infty}h(\tau)d\tau\right)^2\right|\right\rangle,$$

where

$$h(\tau)=3\frac{n_{1x}n_{2x}-n_{1y}n_{2y}}{(1+\tau^2)^{5/2}}+\frac{3n_{1y}n_{2y}-\mathbf{n}_1\mathbf{n}_2}{(1+\tau^2)^{3/2}}+3\frac{n_{1x}n_{2y}+n_{1y}n_{2x}}{(1+\tau^2)^{5/2}}\tau.$$

Numerical integration with a computer yielded $L = 0.05$. The remaining integrals can be calculated analytically:

$$\langle|\xi|\rangle=\pi/8, \quad \langle\xi^2\rangle=\langle\eta^2\rangle=2/9, \quad \langle\xi^2\ln|\xi|\rangle=-0.10.$$

We ultimately get from (13)

$$\sigma=\frac{\pi^3}{16}\frac{d_1d_2}{(j_1j_2)^{1/2}}\frac{1}{\hbar v}\left[1+\frac{8}{9\pi^2}\lambda^2\left(\ln\frac{1}{\lambda^2}-3.64\right)\right]. \tag{14}$$

The cross section σ_{res} at exact resonance is given by (14) with $\lambda = 0$. In the case of a collision between like atoms we have $j_1 = j_2 = j$, $d_1 = d_2 = d$, and $\Delta = 0$ and the excitation-transfer cross section is

$$\sigma=\sigma_{res}=\frac{\pi^3}{16}\frac{d^2}{j\hbar v}.$$

We note the following interesting result. As seen from (14), the excitation-transfer cross section first increases on departing from exact resonance, reaching a maximum at $\lambda \approx 0.1$. Only at $\lambda > 0.16$ does it become smaller than the resonant cross section. The reason for this effect is that the numerator of the interaction operator (2) has a component with alternating sign. The Fourier components of Δ taken for such an expression lead at small Δ to an additional positive rather than negative contribution to the excitation-transfer cross section. The effect does not occur when the interaction Hamiltonian is approximated by an expression of the type CR^{-3}, which contains no alternating-sign component (see [8,9]).

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[1]A. I. Vaĭnshteĭn and V. M. Galitskiĭ, Preprint IYaF SO (Nuc. Phys. Inst., Sib. Div.) AN SSSR (1965); Voprosy teorii atomnykh stolkoveniĭ (Problems in the Theory of Atomic Collisions), Atomizdat (1970), p. 37.
[2]T. Watanabe, Phys. Rev. 138, A 1573 (1965); 140, 5AB (1965).
[3]A. Omont, J. Phys., 26, 26 (1965).
[4]Yu. A. Vdovin and V. M. Galitskiĭ, Voprosy teorii

atomnykh stolkovenii (Problems in the Theory of Atomic Collisions), Atomizdat (1970), p. 65.
[5]Yu. A. Vdovin, N. A. Dobrodeev, V. M. Dubovik, and V. K. Matskevich, ibid. p. 50.
[6]C. G. Carrington, D. N. Stacey and J. Cooper, J. Phys. **B6**, 417 (1973).
[7]V. Weiskopf, Zs. Phys., **34**, 1 (1933).
[8]L. P. Kudrin and Yu. V. Mikhaĭlova, Zh. Eksp. Teor. Fiz. **63**, 63 (1972) [Sov. Phys.-JETP **36**, 33 (1973)].
[9]V Ermatchenko, C. R., Paris, **277**, B 475 (1973).
[10]J. C. Gay and A. Omont, J. de Physique, **35**, 9 (1974).
[11]L. Vaĭnshtein, L. Presnyakov, and Yu. Sobel'man, Zh. Eksp. Teor. Fiz. **43**, 518 (1962) [Sov. Phys.-JETP **16**, 370 (1963)].
[12]L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics), Fizmatgiz (1963), p. 121 [Addison-Wesley, 1965].

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