COLLISIONS OF SLOW HEAVY ATOMS

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The excitation of atoms in slow encounters is studied. If the state of the system of colliding atoms can be represented by a combination of many characteristic states of a quasi-molecule, then excitation of the system will occur in a continuous way as a result of the mixing of newer and newer states of the quasi-molecule and of variation in the statistical weight of the old states. Here statistical theories yielding the mean characteristics of the collisions are applicable, since the excited electron behaves like a classical particle. A criterion which indicates the occurrence of the above excitation mechanism is established for collisions involving heavy atoms.

1. Let us examine the collision of heavy atoms when their relative velocity is much less than the velocity of the atomic electrons. If the probability of excitation of the system is on the order of 1, finding the probability of transition to a definite state is a complicated mathematical problem, since many states must be taken into account in this case. However, the large number of states essential to the calculation of the excitation probability of any given state makes it possible to use a statistical approach in calculating the mean collision characteristics.

The first attempt to do this was made by Russek and Thomas,[1] who suggested that the ionization mechanism was the result of the "evaporation" of electrons from the atoms that had been excited by collision. Experimental parameters were used to support this theory. Also of interest is Firsov's statistical theory of collisions,[2] the results of which are in satisfactory agreement with experimental data. This theory uses a statistical quasi-molecule that consists of Thomas-Fermi atoms, so that the electron motion is regarded as quasi-classical. An electron transfers momentum from one nucleus to another, crossing the equipotential surface of equal action of the nuclei. The energy thus lost by a nucleus is regarded as expended on electron excitation.

The authors of both papers suggest that the excitation of the atoms is to be assumed to occur continuously, just as though the excited electrons were classical and possessed a continuous energy spectrum. In the present article this suggestion is proved correct. In addition, the mechanism of atomic excitation and ionization is discussed.

2. Let us expand the Ψ-function of a system of colliding atoms in terms of the eigenfunctions ψ_m of a quasi-molecule (the quasi-molecule being a system of the same atoms with nuclei at rest). Thus

$$\Psi = \sum_m C_m (t)\, \psi_m \exp\left(-i\int^t E_m\, dt'\right), \qquad (1)$$

where E_m is the eigenvalues of the states of the quasi-molecule. We use a system of atomic units where $\hbar = m_e = e^2 = 1$. Substituting (1) into the Schrödinger equation $i\partial\Psi/\partial t = H\Psi$, we obtain the following system of equations for the coefficients[3]

$$\dot{C}_k = \sum_m \left(\frac{\partial}{\partial t}\right)_{mk} C_m \exp\left(i\int^t \omega_{km}\, dt'\right), \qquad \omega_{km} = E_k - E_m. \quad (2)$$

Let us consider the case where the correlation of two states

$$\dot{C}_1 = \left(\frac{\partial}{\partial t}\right)_{21} \exp\left(i\int^t \omega_{12}\, dt'\right) C_2,$$

$$\dot{C}_2 = -\left(\frac{\partial}{\partial t}\right)_{21} \exp\left(-i\int^t \omega_{12}\, dt'\right) C_1$$

is important in the system (2). The frequency ω of the transition from one state to another is $\sim (\partial/\partial t)_{12}$, and the transition is possible if the phase in the exponent has no time to change within the time $1/\omega$, i.e., if $(\partial/\partial t)_{12} \gtrsim \omega_{12}$. When this condition is fulfilled, the state of the moving atoms becomes a combination of the two quasi-molecular characteristic states whose statistical weights coincide as to order of magnitude and vary in time.

Obviously, the situation is the same when there is a correlation between many states. States k and

m correlate if the relation $(\partial/\partial t)_{km} \gtrsim \omega_{km}$ is fulfilled. In this case the state of the moving atoms becomes a superposition of a large number of quasi-molecule states in which each of the states is noticeably represented. Because of the translation of the nuclei there occurs an "intermixing" of newer and newer states of the quasi-molecule. This causes a shift of the energy "center of gravity" of the quasi-molecular states, and the shift occurs continuously.

3. Thus, if the state of a system of colliding atoms is the superposition of a large number of characteristic quasi-molecular states, a statistical model is applicable to the study of atomic ionization. In this case the electrons behave like classical particles (their mean energy changing continuously). This condition may be written as

$$\Delta E \gg \omega_{12}, \quad \Delta E = \sqrt{\langle H^2 \rangle - \langle H \rangle^2}, \quad (3)$$

where ω_{12} is the excitation energy.

Now let us compute ΔE for the case of collisions of heavy atoms. In a quasi-molecule composed of atoms an electron is generally situated near one of the atoms. Therefore, all of space breaks up into two regions, in each of which electrons strongly interact with a corresponding nucleus.[2] Accordingly, the electronic wave function Φ (in the single-electron approximation) can be represented as

$$\Phi = \prod_k [\chi_k(|\, r_k - R_1|) + \varphi_k(|\, r_k - R_2|)] \exp\left(\sum_k i v_k r_k\right)$$

$$= \Psi \exp\left(\sum_k i v_k r_k\right),$$

where R_1 and R_2 are the coordinates of the nuclei, r_k and v_k are the coordinate and mean velocity of the k electron, and χ and φ are the wave functions of the electron in the field of one or the other of the nuclei. For internal electrons one of these functions is always zero. The Hamiltonian for the electron system has the form

$$H = \sum_k \frac{p_k^2}{2} + u_{int} + i v_1 \frac{\partial}{\partial R_1} + i v_2 \frac{\partial}{\partial R_2}$$

$$= H_0 + i v_1 \frac{\partial}{\partial R_1} + i v_2 \frac{\partial}{\partial R_2},$$

where v_1 and v_2 are the velocities of the nuclei, u_{int} is the interaction term which accounts for the self interaction of the electrons as well as the interactions between electrons and nuclei, and $i v_1 \cdot \partial/\partial R_1 + i v_2 \cdot \partial/\partial R_2$ represents the translational motion of the electrons together with the nuclei.

Hence for the value of ΔE^2 we obtain the formula

$$\Delta E^2 = \langle H^2 \rangle - \langle H \rangle^2 = \langle \Psi \,|\, H_0^2 \,|\, \Psi \rangle - \langle \Psi \,|\, H_0 \,|\, \Psi \rangle^2$$

$$+ \sum_k \{ \langle \chi_k \,|\, [(v_1 - v_k)\, p_k]^2 \,|\, \chi_k \rangle + \langle \varphi_k \,|\, [(v_2 - v_k)\, p_k]^2 \,|\, \varphi_k \rangle \}$$

Since H_0 and Ψ correspond to the stationary state of the quasi-molecule, we have $\langle \Psi \,|\, H_0^2 \,|\, \Psi \rangle - \langle \Psi \,|\, H_0 \,|\, \Psi \rangle^2 \equiv 0$. Averaging over the electron momenta and making use of the fact that

$$\int_{-1}^{1} P_l^2 (\cos \theta) \cos^2 \theta \; d \cos \theta = \frac{1}{2} + \frac{1}{2(2l-1)(2l+3)} \approx \frac{1}{2}$$

we find that

$$\Delta E^2 = \sum_k \left[(v_1 - v_k)^2 \left\langle \chi_k \,\middle|\, \frac{p_k^2}{2} \,\middle|\, \chi_k \right\rangle + (v_2 - v_k)^2 \left\langle \varphi_k \,\middle|\, \frac{p_k^2}{2} \,\middle|\, \varphi_k \right\rangle \right].$$

It is evident that the internal electrons do not contribute to ΔE^2. Therefore, as $R \to \infty$ (R being the distance between the nuclei), when every electron moves with a nucleus in whose field it is entirely situated, we have $\Delta E^2 = 0$. The nonstationarity of ΔE^2 is mostly due to electrons that have ceased to be internal and hence undergo transitions from one atom to another but that have not had time to become sufficiently excited, so that their orbits are of the same order as the distance between the nuclei. Excited electrons contribute only slightly to ΔE^2.

To evaluate ΔE^2 we use a classical model of the quasi-molecule. Thus $\Delta E^2 = v^2 \sum_k T_k$, where

T_k is the kinetic energy of the electrons that penetrate the effective range of one of the atoms with the mean velocity of the other atom. Entering the effective range of the other atom, an electron collides inelastically with the electrons of this atom until its mean velocity becomes equal to that of the other electrons in this region. Since the mean energy of the electrons in this region is maintained by the corresponding nucleus, the energy received in this case by the electrons is taken from the nuclei.

The electrons which transfer momentum from one nucleus to another are situated within a narrow region whose size is on the order of the free path length $\lambda \sim n^{-1/3}$ (n being the electron density), hence

$$\Delta E^2 = \int \frac{p^2}{2} n \, dS \, dx = \int \frac{p^2}{2} n \lambda \, dS \sim \int n \, \frac{p}{4} \, dS = \frac{dE}{dt},$$

where S is the plane separating the action regions of the atoms. Thus, for the model used $\Delta E^2 \sim dE/dt$, which is in agreement with the uncertainty principle. Applying Firsov's results,[2] we

obtain

$$\Delta E^2 \sim v^2 Z^{4/3} R^{-2}, \qquad (4)$$

where $Z = Z_1 + Z_2$ (the nuclear charges Z_1 and Z_2 are of the same order; in the region of interest the Thomas-Fermi potential is $\chi(x) \sim x^{-1}$, with $x = 1.13 Z^{1/3} R$).

Nuclear separations for which Eq. (3) applies, so that the electron excitation is continuous, are obtained if the condition

$$v \gg (\omega^2 Z^{1/3} \mu^{-1})^{1/4} \qquad (5)$$

is satisfied (here we have taken the atomic interaction potential[4] $u \sim Z^{5/3} R^2 \sim \mu v^2$ where μ is the mass of the incoming atom).

The excitation energy ω of the quasi-molecule is ordinarily less than the corresponding atomic quantity, for when R is on the order of the atomic dimensions, there is an abrupt rearrangement of the electronic shells of the quasi-molecule. If the state of the system corresponds from the very beginning to the excited state of the quasi-molecule, then the statistical ionization theory is applicable up to the ionization threshold.

4. Thus, by applying (3) and (4) we find that when heavy atoms collide, there is a rather wide range of relative collision velocities, given by Eq. (5), or

$$\omega Z^{-1/3} \ll v \ll 1 \qquad (6)$$

(here $R \sim 1$), in which the excitation occurs continuously because of the exchange of electrons with different mean velocities. The continuity of the excitation also makes it possible to describe the ionization in the classical way.[1,2,5] The classical description becomes the correct one when the quasi-molecular ground and excited states enter into the state of the moving system with statistical weights that have the same order of magnitude. The mean excitation energy can be calculated directly from the adiabatic system of equations (2) by assuming the electron spectrum to be continuous and by introducing the probability of finding an electron in the given energy interval.

In studying the excitation of colliding atoms it is essential to establish how the experimentally determined[6-8] inelastic energy loss is expended. If an electron is sufficiently excited, then when the dimensions of the electron orbits greatly exceed the distances between the nuclei, the value of ΔE diminishes, and the probability that the electron will be in a given energy interval is described by an equation of the diffusion type (just as in the case of recombination[9]). Therefore, the energy distribution of the ionized electrons falls off sharply with increase in their energy. This is in agreement with experimental data.[10-13] When the relative collision velocities are small, autoionization may be important. This brings about additional maxima in the energy distribution of the ionized electrons.

There is little probability of emission during a collision. The typical period of emission[14] when an electron passes to the ground state $\tau_{emis} \sim \omega^3 c^{-3} |d_{0k}|^2 \le \omega^2 / c^3$ is much longer than the collision time $\tau_{coll} \sim v^{-1}$, at least up to excitation energies $\omega \sim 10$. Thus, the inelastic energy loss is mostly expended on electron excitation up to ionization.

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28