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ELECTRON TRANSITIONS IN CHEMICAL REACTIONS

B. M. SMIRNOV

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Reactions of the H + H_2 type are considered, where the proton can be substituted by any other positive singly charged particle. The electron energy levels of the two states of the H_3 system intersect when the nuclei from an equilateral triangle. When a hydrogen atom is removed to infinity one of the states corresponds to a hydrogen molecule and the other to a triplet state of two hydrogen atoms. In the case of interaction the atom and molecule interaction potential is of the order of 1 eV. The electron transition cross section in collisions between the atom and molecule is $\sigma = \sigma_0\sqrt{v}$ where σ_0 is of the order of an atomic dimension and v is the relative collision velocity in atomic units. The atomic transition results in a sharp redistribution of the energy between the nuclei. This is especially important in the substitution reaction between muonium and a hydrogen molecule.

In the description of chemical reactions it is usually assumed that the reaction depends on the character of motion of the nuclei in the field produced by the interaction between molecules [1]. The electron distribution is taken into account when determining the molecule interaction potential. It is assumed in this case that upon collision of the molecules there are no transitions between the electron states. However, the electron energy levels, which depend in a complicated manner on the distances between nuclei, can intersect for certain nuclear configurations. If such configurations or configurations close to them are produced by the nuclei upon collision of the molecules, then an electron transition occurs and this is appreciably reflected in the course of the chemical reaction. We shall consider the influence of an electronic transition on the simplest type of reaction, that between the hydrogen atom and the hydrogen molecule (in which reaction the proton can be replaced by a deuteron or by a positive muon).

The general properties of a system consisting of three hydrogen atoms were investigated in several works [2-4]. The potential of the interaction between the atom and the molecule of hydrogen was calculated by perturbation theory under the assumption that the ratio of the Coulomb and exchange parts of the interaction energy remains constant when the distance between nuclei changes [5]. This method gives a rough idea of the variation of the interaction potential only at large distances between the atom and the molecule. Some properties of the interaction potential at medium distances can be obtained from general considerations.

The Ψ functions of the eigenstates of the system in the one-electron approximation can be written in the form of a linear combination of Slater determinants [6]:

$$\Phi_1 = \begin{vmatrix} \psi_a(1)\,\eta_-(1) & \psi_a(2)\,\eta_-(2) & \psi_a(3)\,\eta_-(3) \\ \psi_b(1)\,\eta_+(1) & \psi_b(2)\,\eta_+(2) & \psi_b(3)\,\eta_+(3) \\ \psi_c(1)\,\eta_+(1) & \psi_c(2)\,\eta_+(2) & \psi_c(3)\,\eta_+(3) \end{vmatrix},$$

$$\Phi_2 = \begin{vmatrix} \psi_a(1)\,\eta_+(1) & \psi_a(2)\,\eta_+(2) & \psi_a(3)\,\eta_+(3) \\ \psi_b(1)\,\eta_-(1) & \psi_b(2)\,\eta_-(2) & \psi_b(3)\,\eta_-(3) \\ \psi_c(1)\,\eta_+(1) & \psi_c(2)\,\eta_+(2) & \psi_c(3)\,\eta_+(3) \end{vmatrix},$$

$$\Phi_3 = \begin{vmatrix} \psi_a(1)\,\eta_+(1) & \psi_a(2)\,\eta_+(2) & \psi_a(3)\,\eta_+(3) \\ \psi_b(1)\,\eta_+(1) & \psi_b(2)\,\eta_+(2) & \psi_b(3)\,\eta_+(3) \\ \psi_c(1)\,\eta_-(1) & \psi_c(2)\,\eta_-(2) & \psi_c(3)\,\eta_-(3) \end{vmatrix}.$$

Here $\psi_a(i)$, $\psi_b(i)$, and $\psi_c(i)$ are the coordinate wave functions of the i-th electron, which is situated near the given nucleus; η_+ and η_- are the spin functions of the electron with corresponding sign of the spin projection on the preferred direction. We shall assume that the distance between the nuclei a and b is conserved.

In the investigation of the electron energy levels, the nuclei serve as Coulomb centers.

Assume that the nuclei form an "isosceles triangle" with nucleus c at the vertex. Then the plane passing through the altitude of the triangle and perpendicular to it is the symmetry plane of the system. For the system obtained when three hydrogen atoms are reduced to the ground state, reflection relative to the symmetry plane yields

$$\psi_a \to \psi_b, \qquad \psi_b \to \psi_a, \qquad \psi_c \to \psi_c.$$

Whence we find that upon reflection

$$\Phi_1 \to -\Phi_2, \quad \Phi_2 \to -\Phi_1, \quad \Phi_3 \to -\Phi_3.$$

Therefore there is an even eigenfunction, which conserves its sign upon reflection: $C_1(\Phi_1 - \Phi_2)$, and two odd eigenfunctions: $C_2(\Phi_1 + \Phi_2) + C_3\Phi_3$ and $C_3(\Phi_1 + \Phi_2) - C_2\Phi_3$.

When the nucleus c moves away to infinity, the even state corresponds to the hydrogen molecule ab, while the odd ones go over into the triplet state of the atoms a and b. For finite distances between nuclei, the odd states have a nodal surface ($|\psi|^2 = 0$) as the symmetry plane. Therefore the electrons in the odd state are distributed in a larger region and have a smaller binding energy than in the even state. If the nuclei form an equilateral triangle, a new symmetry property appears. The operator of rotating the system through 120° about the center of the triangle commutes with the Hamiltonian, so that the eigenfunctions can be resolved in terms of the eigenvalues of this operator. Upon rotation $\psi_a \to \psi_c$, $\psi_b \to \psi_a$, and $\psi_c \to \psi_b$. By virtue of symmetry, ψ_a, ψ_b, and ψ_c are identical functions. Therefore upon rotation $\Phi_1 \to \Phi_2$, $\Phi_2 \to \Phi_3$, and $\Phi_3 \to \Phi_1$.

In determining the eigenfunctions of the rotation operator $\hat{\alpha}$ we make use of the fact that as a result of three rotations the system returns to the initial state. Therefore $\alpha^3 = 1$ and the eigenvalues of the operator $\hat{\alpha}$ are 1, $\exp(2i\pi/3)$, and $\exp(-2i\pi/3)$. The corresponding eigenfunctions are $\Psi = a_1\Phi_1 + a_2\Phi_2 + a_3\Phi_3$ and are determined from

$$\hat{\alpha}\Psi = a_1\Phi_2 + a_2\Phi_3 + a_3\Phi_1 = \alpha\,(a_1\Phi_1 + a_2\Phi_2 + a_3\Phi_3).$$

They have the form

$$\begin{aligned}\Psi_{\rm I} &= C_{\rm I}\,(\Phi_1 + \Phi_2 + \Phi_3),\\ \Psi_{\rm II} &= C_{\rm II}\,[\Phi_1 + \Phi_2 \exp(2i\pi/3) + \Phi_3 \exp(-2i\pi/3)],\\ \Psi_{\rm III} &= C_{\rm II}\,[\Phi_1 + \Phi_2 \exp(-2i\pi/3) + \Phi_3 \exp(2i\pi/3)];\end{aligned}$$

$C_{\rm I}$ and $C_{\rm II}$ are normalization constants. Since $\Psi_{\rm II} = \Psi^*_{\rm III}$, we get

$$E_{\rm II} = \langle \Psi^*_{\rm II} H \Psi_{\rm II}\rangle = \langle \Psi^*_{\rm III} H \Psi_{\rm III}\rangle^*$$

$$= E_{\rm III} \quad (\text{H — Hamiltonian of the electrons}),$$

$$\Psi_{\rm II} = C_{\rm II}\,[(\Phi_1 - \Phi_2) - \exp(-2i\pi/3)\,(\Phi_2 - \Phi_3)],$$

that is, $\Psi_{\rm II}$ and $\Psi_{\rm III}$ correspond to combinations of even functions. $\Psi_{\rm I}$ is an odd function relative to reflection about any symmetry plane. Therefore $E_{\rm I} > E_{\rm II} = E_{\rm III}$, that is, for a given nuclear configuration the energy level of the ground state is crossed. It is easy to show that the energy-difference surface has near the point of intersection the form of a cone and that the eigenfunctions of the Hamiltonian near the intersection point are $(\Psi_{\rm II} + \Psi_{\rm III})/2$ and $(\Psi_{\rm II} - \Psi_{\rm III})/2$.

Let us calculate the probability of the electron transition upon collision between a hydrogen atom (or some other similar atom) and a hydrogen molecule. We shall assume that the nuclei a and b remain stationary during the time of collision, corresponding to a large velocity of the incident particle compared with the velocity of the oscillation of the nuclei in the molecule. The probability of an electron transition with a single passage through the pseudointersection point is determined by the Landau-Zener formula[7]

$$W = \exp\,[-\,2\pi\Delta^2/v_R\,|F_{12}|],$$

where Δ — minimum energy difference corresponding to motion along a given trajectory, and $F_{12} = \delta(E_{\rm II} - E_{\rm III})/\delta R$. (We use a system of atomic units $\hbar = m_{el} = e^2 = 1$). We shall assume that the points of intersection of the levels are readily attained and that the energy-difference cone has a circular base near the points of intersection, that is, $\Delta E = \beta\,|\mathbf{R} - \mathbf{R}_0|$, where $\mathbf{R}_0$ is the point of intersection. Then ($F_{12} = \beta$)

$$W = \exp\,(-\,2\pi\beta\rho^2/v\cos\theta),$$

where ρ is the impact parameter and θ the angle between the direction of the trajectory and the line of intersection of the energy levels in the transition region.

The cross section of the transition is

$$\sigma = \frac{2}{\pi}\int_0^{\pi/2} l(\varphi)\,d\varphi \cdot 2\int_0^{\infty} d\rho \int_0^1 W d\cos\theta,$$

$$l(\varphi) = 4R_0 \int_0^{\pi/2} \sqrt{1 - \sin^2\alpha\,\sin^2\varphi}\,d\alpha,$$

where $l(\varphi)$ is the length of the projection of the circle where the terms cross on the plane perpendicular to the direction of the beam, $R_0 = R_{ab}\sqrt{3/2}$ is its radius, and R_{ab} is the distance between the nuclei in the molecule. We have

$$\int_0^{\pi/2} \frac{2}{\pi}\,l(\varphi)\,d\varphi$$

$$= \frac{R_0}{\pi}\left[4K^2\left(\frac{\pi}{2}, \frac{1}{\sqrt{2}}\right) + \pi^2/K^2\left(\frac{\pi}{2}, \frac{1}{\sqrt{2}}\right)\right] \approx 5.3\,R_0,$$

where K — elliptic integral. Since

$$I(\gamma) = \int_{-\infty}^{+\infty} d\rho \int_0^1 dx e^{-\gamma\rho^2/x} = 2\sqrt{\pi}/3\gamma^{1/2},$$

we have $\sigma = 2.49\,R_0\sqrt{v/\beta}$. The value of β is smaller than unity. We ultimately obtain

$$\sigma = \sigma_0\sqrt{v} \quad (\sigma_0 = 3.02/\beta^{1/2}),$$

where σ_0 is of the order of the atomic value.

It is important to know at what collision energies an electron transition is possible, that is, what is the potential of interaction of the atom and the molecule that corresponds to the nuclear configuration at which the electron terms cross. Since the interaction potential cannot be calculated, we estimate it by means of perturbation theory. We assume that the energy of the three-atom system is an additive function of the interaction energies of the atoms and that the electron distribution near each atom is the same as in the hydrogen atom. Under these assumptions, the interaction energy (with the energy of the isolated molecule and of the hydrogen atom taken as zero) in all three states is $\epsilon_{tr} - D$, where D is the hydrogen molecule dissociation energy and ϵ_{tr} is the repulsion energy of the two hydrogen atoms in the triplet state. In states whose energy levels cross, the interaction constant can be even smaller. On the basis of the data obtained in [8], we have for the hydrogen molecule $\epsilon_{tr} - D \approx 1$ eV. Thus, the electronic transition is significant at collision energies larger than 1 eV.

If the collision between the atom and molecule in question is accompanied by an electron transition and the atom c goes to infinity, then the atoms a and b remain in the triplet state, which leads to a disintegration of the molecule. Thus, an electronic transition is accompanied by a sharp redistribution of the energy between the nuclei, and possibly makes an appreciable contribution to the dissociation cross section. The redistribution of the energy in an electronic transition is particularly important in collisions between muonium (hydrogen atom whose nucleus is a positive muon) and a hydrogen molecule. Upon collision with a hydrogen molecule, the positive muon, being a light particle (with mass 208), cannot transfer a noticeable part of its energy to the protons, so that the substitution reaction with formation of μ-hydrogen molecule as a result of the transition of heavy particles has low probability. If collision is accompanied by electronic transition and the energy of the incident muonium is smaller than $\epsilon_{tr} + D_{tr} \approx 11$ eV, the muonium cannot leave the field of attraction of the hydrogen atoms. In the new state, corresponding to a different atomic interaction potential, the distance between the atoms of the hydrogen increases. Following the inverse electronic transition, the probability of emission of the hydrogen atom and of the formation of a μ-hydrogen molecule is close to unity.

In conclusion we note that the described electronic transition mechanism appears in the case of a chemical reaction between any atom and a diatomic molecule made up of the same atoms.

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