

## EXCITATION TRANSFER IN ATOMIC COLLISIONS

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Submitted to JETP editor January 22, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) 51, 466-474 (August, 1966)

Asymptotically exact term splitting for an excited atom interacting with another atom is calculated for large internuclear distances. The result is used to determine the cross section for excitation transfer from a metastable atom to an identical atom in its ground state. The diffusion coefficient for metastable atoms in their own gas is calculated.

1. THE processes involved in large transition cross sections are of the greatest interest in the physics of atomic collisions. Whenever a transition cross section is determined mainly by an impact parameter that is much larger than the dimensions of the colliding atoms, the magnitude of the cross section is associated with the asymptotic value of the difference between terms of the quasimolecule formed by the colliding atoms. Thus the cross section for resonance charge exchange between an ion and a parent atom is expressed in terms of the difference between an even- and odd-state term of the quasimolecule composed of the given ion and atom,<sup>[1]</sup> the cross section for electron transfer between two atoms of spin  $1/2$  is determined by the difference between singlet and triplet states of the quasimolecule,<sup>[2]</sup> the cross section for excitation transfer in the collision of a resonantly excited atom with an identical atom is associated with the dipole interaction of the colliding atoms,<sup>[3]</sup> and the cross section for a transition between fine-structure components of an excited atom is determined by the splitting of its terms as a result of interaction with another atom.<sup>[4]</sup>

In calculating the asymptotic difference between terms of a quasimolecule that consists of two atomic particles separated by a distance much larger than the atomic dimensions, two extremely opposite cases must be distinguished. In the first case the range of action of the two atoms, which determines the term splitting, is of the same order as the interatomic distance. This applies to the first two of the foregoing examples, for which the method of determining the asymptotic difference of terms is given in <sup>[5, 6]</sup>. In the second case the range of the atoms is much smaller than their separation; this applies to the last two cases. Here one calculates for an excited atom the term shift induced by its interaction with another atom that is in its ground state (or in a weak state of excitation). This problem has been solved by Ovchinni-

kova<sup>[7]</sup> assuming that the electron wave function in an excited atom changes only slightly in distances of the order of the radius of the perturbing atom. This hypothesis breaks down, however, for the cross section of a transition between fine-structure components of a resonantly excited alkali metal atom that has collided with an inert-gas atom. In the present work we have calculated the asymptotic shift of excited-atom terms that results from interaction with another atom, without employing the foregoing hypothesis. The result of this calculation is used to obtain the cross section for excitation transfer resulting from the collision between a metastable atom and an atom in its ground state.

2. We shall calculate the change in the binding energy of an atomic electron as a result of its interaction with another atom. It will be assumed that the interatomic distance  $R$  is much larger than the atomic radii, so that the relative change of the binding energy will be small. Let  $\Phi(\mathbf{r}_1)$  and  $\Psi(\mathbf{r}_1)$  be the electronic wave function in the excited atom in the absence and presence, respectively, of a perturbing atom; the electronic coordinate  $\mathbf{r}_1$  is measured from the nucleus of the excited atom and  $\gamma^2/2$  is the electronic binding energy. (We shall use the atomic units  $\hbar = m_{e1} = e^2 = 1$ .) Since the interatomic distance is much larger than the radius of the excited atom:

$$R\gamma^2 \gg 1, \quad (1)$$

in the region of the perturbing atom the radial part of the wave function  $\Phi(\mathbf{r}_1)$  coincides with its asymptotic form, so that in this region we have

$$\Phi(\mathbf{r}_1) = \Phi(\mathbf{R}) \exp \left[ - \int_R^{r_1} \left( \gamma^2 - \frac{2}{r'} \right)^{1/2} dr' \right] = \Phi(\mathbf{R}) e^{\beta r \cos \theta}, \quad (2)$$

where  $\beta = \sqrt{\gamma^2 - 2/R}$ ;  $r$ ,  $\theta$ , and  $\varphi$  are the polar coordinates of the electron with their origin in the

nucleus of the perturbing atom, so that for  $r \ll R$  we have

$$r_1 = (R^2 - 2rR \cos \theta + r^2)^{1/2} \approx R - r \cos \theta.$$

The electronic wave function in the atom, in the presence and absence, respectively, of the perturbing atom, satisfies the Schrödinger equations

$$\begin{aligned} -\frac{1}{2}\Delta\Phi + V_0\Phi &= E_0\Phi, \\ -\frac{1}{2}\Delta\Psi + (V_0 + V_1)\Psi &= E\Psi, \end{aligned} \quad (3)$$

where  $E_0 = -\gamma^2/2$ ; the effective potential  $V_0$  includes the interaction with the core of the excited atom, and  $V_1$  describes the interaction between the electron and the perturbing atom ( $V_1 = 0$  outside this atom). We multiply the first of the equations (3) by  $\Psi$  and the second by  $\Phi$ , subtract one from the other, and integrate the difference over the volume outside a spherical surface representing the boundary of the perturbing atom. In this region  $\Psi \approx \Phi$ ; consequently, this region of the coordinates determines the normalization of the wave function,  $\int_V \Psi\Phi \, dr = 1$ , so that

$$E - E_0 = \frac{1}{2} \int_S (\Psi\nabla\Phi - \Phi\nabla\Psi) \, ds_{\text{in}} + \int_V \Psi\Phi V_1 \, dr, \quad (4)$$

where  $ds_{\text{in}}$  is a surface element with its normal directed into the atom.

We shall assume that the field  $V_1(r)$  of the perturbing atom is spherically symmetric. Then for  $r \ll R$  the electronic wave function is expanded in spherical harmonics near the perturbing atom:

$$\begin{aligned} \Phi(r_1) &= \Phi(\mathbf{R}) \frac{1}{2\beta r} \sum_{l=0}^{\infty} (2l+1) P_l(\cos \theta) [\varphi_l^+(r) - \varphi_l^-(r)], \\ \Psi(r_1) &= \Phi(\mathbf{R}) \frac{1}{2\beta r} \sum_{l=0}^{\infty} (2l+1) P_l(\cos \theta) [\psi_l^+(r) - \psi_l^-(r)], \end{aligned} \quad (5)$$

The functions  $\varphi_l$  and  $\psi_l$  satisfy the equations

$$\begin{aligned} \varphi_l'' - \frac{l(l+1)}{r^2} \varphi_l &= \beta^2 \varphi_l, \\ \psi_l'' - \frac{l(l+1)}{r^2} \psi_l + 2V_1(r)\psi_l &= \beta^2 \psi_l, \end{aligned} \quad (6)$$

with  $\varphi_l^+, \psi_l^+ \rightarrow e^{\beta r}$  and  $\varphi_l^-, \psi_l^- \rightarrow e^{-\beta r}$  for  $r \rightarrow \infty$ . Since  $\Psi(\mathbf{r}_1)$  and  $\Phi(\mathbf{r}_1)$  coincide far from the perturbing atom, we have  $\psi_l^+/\varphi_l^+ \rightarrow 1$  for  $r \rightarrow \infty$ . Substituting (5) into (4) and assuming that at the atomic boundary  $V_1 = 0$ , and that  $\varphi_l$  and  $\psi_l$  coincide with their asymptotic expressions:

$$\varphi_l^+ = \psi_l^+ = P_l(1)e^{\beta r}, \quad r\beta \gg 1;$$

$$\varphi_l^- = P_l(-1)e^{-\beta r}, \quad \psi_l^- = [P_l(-1) + c_l]e^{-\beta r}, \quad \beta r \gg 1,$$

we obtain

$$E - E_0 = \frac{\pi}{\beta} \Phi^2(\mathbf{R}) \sum_{l=0}^{\infty} (2l+1) c_l. \quad (7)$$

It can be seen that in (4) the terms of like signs in the exponential will cancel if in (5) we confine ourselves to the first term of each expansion in powers of  $1/r$ . It can be shown that this property is not associated with the approximation that is being used. Indeed, on the basis of (6) it is found that in (4) the terms containing functions with like signs in the exponential will also cancel in the next approximation of the expansion in powers of  $\beta^2 V_1(r)$ . Moreover, it follows from the procedure used to obtain (4) that the given terms will cancel if it is assumed that  $\varphi_l$  and  $\psi_l$  correspond to the same energy. Therefore Eq. (7) is valid if  $|E - E_0| \ll \beta r$  on the boundary of the perturbing atom. However, since  $\Phi^2(\mathbf{R}) \sim e^{-2\beta r}$  this condition is associated with the assumption that the radius of the perturbing atom is much smaller than the interatomic distance  $R$ .

Equation (7) is thus applicable if the radius of the perturbing atom, which is subject to the conditions  $|V_1(r_l)| \ll \beta^2$  and  $r_l \gg l/\beta$ , is much smaller than the interatomic distance ( $r_l \ll R$ ). The first of these two conditions is fulfilled when the ionization potential of the perturbing atom is smaller than the binding energy of the electron in the excited atom. The second condition is violated when  $l$  is large. However, the large angular momentum terms contribute little to (7), so that this circumstance does not affect the accuracy of the result.

3. The derived result (7) corresponds to the term shifts that are calculated when the wave function of the unperturbed atom is not zero at the location of the perturbing atom  $\Phi(\mathbf{R}) \neq 0$ . We shall calculate the level shifts for the case in which the projection of the electronic angular momentum on the internuclear axis is unity. Then near this axis  $\Phi(\mathbf{r}_1) = \chi(r_1) \sin \vartheta e^{i\epsilon}$ , where  $r_1$ ,  $\vartheta$ , and  $\epsilon$  are the spherical coordinates of the electron, with the origin in the nucleus of the unperturbed atom and the internuclear line as the polar axis. For polar coordinates  $r$ ,  $\theta$ , and  $\epsilon$  measured from the nucleus of the perturbing atom we obtain near the latter (for  $r \ll R$ )

$$\begin{aligned} \Phi(\mathbf{r}_1) &= \chi(R) e^{\beta r \cos \theta} \frac{r}{R} \sin \theta e^{i\epsilon} \\ &= \frac{\chi(R)}{R} e^{i\epsilon} \sum_{l=1}^{\infty} \frac{(2l+1)}{2\beta^2 r} P_l^{(1)}(\cos \theta) [\varphi_l^+(r) - \varphi_l^-(r)], \end{aligned} \quad (8a)$$

where  $\varphi_l^+$  and  $\varphi_l^-$  satisfy (6) and have the asymp-

otic forms  $\varphi_l^+ \rightarrow e^{\beta r}$  and  $\varphi_l^- \rightarrow e^{-\beta r}$  for  $r \rightarrow \infty$ . The spherical-harmonic expansion of  $\psi(\mathbf{r}_1)$ , which coincides with  $\Phi(\mathbf{r}_1)$  far from the perturbing atom, is

$$\Psi(\mathbf{r}_1) = \frac{\chi(R)}{R} \frac{1}{2\beta^2 r} \sum_{l=1}^{\infty} (2l+1) e^{i\epsilon} \times P_l^{(l)}(\cos \theta) [\psi_l^+(r) - \psi_l^-(r)], \quad (8b)$$

The  $\psi_l$  functions satisfy (6), so that their asymptotic expressions are again  $\psi_l^+ \rightarrow e^{\beta r}$ , and  $\psi_l^- \rightarrow [(-1)^l + c_l] e^{-\beta r}$  for  $r \rightarrow \infty$ . Substituting the expansions (8a) and (8b) into (4) (with  $\Phi$  replaced by  $\Phi^*$ ), we obtain for the energy shift

$$E - E_0 = \frac{\pi}{\beta^3 R^2} \chi^2(R) \sum_{l=1}^{\infty} (2l+1) c_l. \quad (9)$$

4. We shall now calculate the coefficients  $c_l$  that are used to represent the shifts of levels in (7) and (9). To this end we must solve (6) for  $\psi_l$  and determine the asymptotic behavior of the electronic radial wave function far from the atom:

$$\psi_l \xrightarrow{r \rightarrow \infty} [e^{\beta r} + (-1)^l e^{-\beta r} + c_l e^{-\beta r}]$$

$$= \sqrt{2\pi} \beta r \left[ I_{l+1/2}(\beta r) + \frac{c_l}{\pi} K_{l+1/2}(\beta r) \right].$$

In the case being considered here the electronic binding energy  $\beta^2/2$  in the excited atom is much smaller than the ionization potential of that atom, so that  $c_l$  can be expanded in a series with respect to  $\beta$ . Moreover, for small  $\beta$  the dependence of  $c_l$  on  $\beta$  is determined by the long-range polarization potential; therefore, to obtain the dependence of  $c_l$  on  $\beta$  it is sufficient to solve the equation

$$\left( \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + \frac{\alpha}{r^4} - \beta^2 \right) \psi_l = 0, \quad (10a)$$

where  $\alpha$  is the polarizability of the perturbing atom. For small  $\beta$  we divide the coordinate space into two regions. In the first region we have  $r \ll \sqrt{l(l+1)}/\beta$ , ( $r \ll 1/\beta$  for  $l=0$ ), and the term  $\beta^2 \psi_l$  can be neglected in comparison with the terms  $\psi_l''$  and  $l(l+1)r^{-2} \psi_l$ . In the second region  $r \gg (\alpha/l(l+1))^{1/2}$ , ( $r \gg \sqrt{\alpha}$  for  $l=0$ ), so that  $\alpha r^{-4} \psi_l$  is much smaller than  $l(l+1)/r^2$  and  $\psi_l''$ . If  $\alpha\beta^2 \ll l(l+1)$ , ( $\alpha\beta^2 \ll 1$  for  $l=0$ ), these regions overlap. Therefore, by connecting the asymptotic solutions at the boundary between the two regions we are enabled to express the coefficients  $c_l$  in terms of the parameters of (10a) and the boundary conditions.

For

$$[\alpha/l(l+1)]^{1/2} \ll r \ll [l(l+1)/\beta^2]^{1/2} \\ (\sqrt{\alpha} \ll r \ll 1/\beta \text{ for } l=0)$$

the electronic wave function corresponding to the asymptotic solution in the second region ( $r \ll \sqrt{l(l+1)}/\beta$ ,  $\beta^{-1}$ ) is

$$\psi_l = \frac{2(\beta r)^{l+1}}{(2l+1)!!} + c_l \frac{(2l-1)!!}{(\beta r)^l}.$$

We shall compare this solution with the solution of the equation that differs from (10a) with respect to the sign of  $\beta^2$ , describes a free electron, and was investigated in [8]:

$$\left[ \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + \frac{\alpha}{r^4} + \beta^2 \right] \xi_l(r) = 0. \quad (10b)$$

For large  $r$  ( $r \gg \beta^{-1} \sqrt{l(l+1)}$ ,  $\beta^{-1}$ ) the solution of this equation becomes\*

$$\xi_l(r) = (\pi\beta r)^{1/2} [J_{l+1/2}(\beta r) - (-1)^l J_{l-1/2}(\beta r) \operatorname{tg} \delta_l],$$

where  $\delta_l(\beta)$  is the phase shift for an electron with the energy  $\beta^2/2$  scattered elastically on the perturbing atom. For small  $r$  we have

$$[\alpha/l(l+1)]^{1/2} \ll r \ll \beta^{-1} \sqrt{l(l+1)}$$

(or  $\sqrt{\alpha} \ll r \ll \beta^{-1}$  for  $l=0$ ), and the solution of (10b) becomes

$$\xi_l(r) = \frac{2(\beta r)^{l+1}}{(2l+1)!!} - \frac{2 \operatorname{tg} \delta_l (2l-1)!!}{(\beta r)^l}.$$

To obtain the functions  $c_l(\beta)$  and  $2 \tan \delta_l(\beta)$  we must solve (10a) and (10b) for small  $r$  ( $r \ll \sqrt{l(l+1)}/\beta$ ,  $\beta^{-1}$ ) with given boundary conditions, i.e., with a given procedure for taking into account the short-range potential of interaction between an electron and the perturbing atom. If in this region of  $r$  the term  $\beta^2 \psi_l$  ( $\beta^2 \xi_l$ ) is neglected in (10a) and (10b), then from the boundary condition for  $\psi_l$ , which is  $\xi_l \rightarrow \text{const} \cdot (r^{l+1} - \kappa^2 l^{l+1} r^{-l})$  for  $r \rightarrow 0$ , we obtain the relations of  $c_l^{-1}$  and  $1/2 \cot \delta_l$  to the scattering length; the two quantities are expressed alike in terms of the scattering length ( $\delta_l \sim \beta^2 l^{l+1}$ ). For zero phase shift and the coefficient  $c_0$ , by taking the boundary condition into account we obtain the first term in the expansion of each quantity with respect to  $\beta$ ; these first terms are identical for  $c_0^{-1}$  and  $1/2 \cot \delta_l$ . To obtain the second terms of the respective expansions the

\* $\operatorname{tg} \equiv \tan$ .

term  $-\beta^2\psi_l$  in (10a) and  $\beta^2\xi_l$  in (10b) will be regarded as perturbations in the given coordinate region. Therefore the second terms of the expansions of  $c_0^{-1}$  and  $\frac{1}{2}\cot\delta_l$  with respect to  $\beta$  have opposite signs. By the same procedure we can obtain the relation between higher terms of the expansions of  $c_0^{-1}$  and  $\frac{1}{2}\cot\delta_l$  with respect to  $\beta$ .

Using the expansion of  $\cot\delta_0(\beta)$  for small  $\beta$  that is given in [8], we obtain for the zeroth coefficient

$$\frac{2\beta^2}{c_0} = \frac{\beta}{L} + \frac{\pi\alpha}{3L^2}\beta^2 + \frac{4\alpha}{3L}\beta^3\ln\frac{\beta\alpha}{4}, \quad (11a)$$

where  $L$  is the scattering length for the electron interacting with the perturbing atom. To obtain  $c_l$  with  $l \neq 0$  it is sufficient to limit these quantities to the first term of the expansion in  $\beta$  that is obtained by considering  $\beta^2\psi_l$  as a perturbation in (10a). From a comparison with the expansion of  $\tan\delta_l(\beta)$  in [8] we obtain

$$c_l = 2\pi\alpha\beta^2 / (2l+3)(2l+1)(2l-1). \quad (11b)$$

Substituting (11) into (7) and (9), we obtain for the level shift when the wave function of the unperturbed atom does not vanish on the internuclear axis

$$E - E_0 = 2\pi\Phi^2(\mathbf{R}) \left[ \left( \frac{1}{L} + \frac{\pi\alpha}{3L^2}\beta + \frac{4\alpha}{3L}\beta^2\ln\frac{\beta\alpha}{4} \right)^{-1} + \frac{\pi\alpha\beta}{3} \right], \quad (12a)$$

and also when it vanishes as  $\sin\vartheta$  [where  $\vartheta$  is the polar angle measured from the internuclear axis with the coordinate origin at the nucleus of the principal (excited) atom] we have

$$E - E_0 = \frac{2\pi\alpha}{3\beta R^2} \lim_{r_1 \rightarrow \mathbf{R}} \left| \frac{\Phi(\mathbf{r}_1)}{\sin\vartheta} \right|^2. \quad (12b)$$

Thus, independently of the interatomic distance the coefficient in (12a) and (12b) for the asymptotic exchange interaction is represented by an expansion in the small energy of a weakly bound electron. The small parameters of the expansions are  $\beta L \ll 1$  and  $\alpha\beta^2 \ll 1$ ; this can be seen directly from the method used to solve (10a) and (10b) for small  $\beta$ . The small parameter  $\beta L \ll 1$  results from taking into account the boundary condition imposed on the electronic wave function for  $r \rightarrow 0$  and is determined to a large degree by the short-range interaction potential; the small parameter  $\alpha\beta^2 \ll 1$  corresponds to the polarization interaction. The first and second terms in the expansion (11a) are determined by different regions between the electron and nucleus and are therefore not related to

each other. The higher terms of the expansion are much smaller than one of the first two terms, since they contain one of the small parameters to a higher degree. However, the relative magnitudes of the first and second terms can be specified arbitrarily; this procedure was used by O'Malley in [9], where the Ramsauer effect was investigated in electron elastic scattering by inert-gas atoms. Since for small  $k$  the expansion of the phase shift is  $\delta_0 = -Lk - \pi\alpha k^2/3$ , where  $k$  is the electron momentum, the Ramsauer effect should be observed at  $k_0 = -3L/\pi\alpha$ , ( $L < 0$ ); this expansion is valid for  $Lk \ll 1$  and  $\alpha k^2 \ll 1$ , i.e., the Ramsauer effect is expected at low energies. Since this is fulfilled for inert gases, O'Malley [9] used the Ramsauer effect to determine the scattering length for an electron with respect to inert-gas atoms and obtained reliable results.

5. We shall now consider the case of small  $\beta$ . [7] Confining ourselves in (12a) to the first term of the expansion in powers of  $\beta$ , we obtain

$$E - E_0 = 2\pi L\Phi^2(\mathbf{R}), \quad (13)$$

which coincides with the result obtained by Ovchinnikova in [7]. This result is associated with the hypothesis that the electron wave function inside the excited atom does not change within the range of the perturbing atom. Indeed, assuming  $\Phi(\mathbf{r}_1) = \Phi(\mathbf{R})$  and  $\Psi(\mathbf{r}_1) = \Phi(\mathbf{R}) \times [1 - L/r]$  near the perturbing atom and substituting these expressions into (4), we obtain (13).

6. As was mentioned in the introduction, the results in (12a) and (12b) have a relationship to transitions between fine-structure components in collisions between an excited atom and another atom. [4] Thus if the excited atom is an alkali metal in its  $s$ -state the fine-structure states are  $P_{3/2}$  and  $P_{1/2}$  terms, whose difference is determined by the spin-orbit interaction in the atom. The interaction between the excited and perturbing atoms splits the  $P_{3/2}$  into a  $\Sigma$  and a  $\Pi$  term. Since the angular wave function of the  $\Pi$  term vanishes on the internuclear axis, the corresponding energy is independent of the interatomic distance in first approximation. Therefore a collisional transition occurs in the vicinity of a point where the shift of a  $\Sigma$  term equals the energy difference of the corresponding atomic fine-structure components.

The situation described above occurs when the perturbing atom has zero spin. Cases of non-zero spin are accompanied by additional term splitting in accordance with the total spin of the electron and atom. Then Eqs. (12a) and (12b) will contain

the scattering phase shifts corresponding to the same total spin. We here assume that the interatomic distance is not very large, so that the atomic exchange interaction considerably exceeds the van der Waals interaction.

7. We shall now consider one additional process that is related to the result in (12a) and (12b)—excitation transfer in a collision between a metastable atom and an unexcited identical atom. The cross section for this process enables us to determine the diffusion coefficient of the metastable atom in its own gas; this characterizes the lifetime of metastable atoms, which is associated with their drift to the walls. For the sake of simplicity we shall assume zero spin for an atom in its ground state. The quasimolecule consisting of an atom and an excited identical atom is symmetric. Thus the electronic Hamiltonian is not affected by electronic reflection in a symmetry plane perpendicular to the internuclear axis and passing through its midpoint. Therefore the eigenfunctions of the Hamiltonian are even or odd functions depending on whether their sign is conserved or changes with electronic reflection in the symmetry plane. The eigenfunctions of the Hamiltonian for a quasimolecule consisting of an atom and an excited atom are, for large interatomic distances,

$$\Psi_{g,u} = 2^{-1/2}[\Psi_1 \pm \Psi_2].$$

Here  $\Psi_1$  describes the case of an excited atom No. 1 and a ground-state atom No. 2, and vice versa for  $\Psi_2$ . We introduce the functions

$$\Phi_{g,u} = 2^{-1/2}[\Phi_1 \pm \Phi_2],$$

so that  $\Phi_{1,2}$  is defined exactly like  $\Psi_{1,2}$ , except that interatomic interactions are neglected.

We shall employ the procedure that was used to derive (4). The boundaries of the respective atoms will comprise the surface of integration, assuming  $\Phi_1 = \Psi_1$  near the first atom and  $\Phi_2 = \Psi_2$  near the second atom. The result is an equation analogous to (4):

$$E_{g,u} - E_0 = 1/4 \int \{(\Psi_2 - \Phi_2) \nabla \Phi_1 - \Phi_1 \nabla (\Psi_2 - \Phi_2)\} \\ + (\Psi_2 \nabla \Phi_2 - \Phi_2 \nabla \Psi_2) \} ds_{1in} \pm 1/4 \int \{(\Psi_1 - \Phi_1) \nabla \Phi_2 \\ - \Phi_2 \nabla (\Psi_1 - \Phi_1)\} + (\Psi_1 \nabla \Phi_1 - \Phi_1 \nabla \Psi_1) \} ds_{2in}.$$

Neglecting the expressions in square brackets, which are exponentially small compared with the principal term, we obtain

$$E_u = E_0 = E_g - 1/2 \int (\Psi_1 \nabla \Phi_1 - \Phi_1 \nabla \Psi_1) ds_{1in}, \quad (14)$$

where  $E_0$  is the atomic interaction energy, and  $E_g$  and  $E_u$  are the even and odd states of the

quasimolecule. It then follows from a comparison of (14) and (4) that the difference between the even and odd quasimolecular states is given by (4) and (12).

The wave function of a quasimolecule consisting of a ground-state and an excited atom, corresponding to excitation of the first atom before the collision, is, for slow nuclear motion,

$$\Psi = \frac{1}{\sqrt{2}} \Psi_g \exp \left\{ -i \int_{-\infty}^{+\infty} E_g dt' \right\} \\ + \frac{1}{\sqrt{2}} \Psi_u \exp \left\{ -i \int_{-\infty}^{+\infty} E_u dt' \right\}.$$

This expression satisfies the Schrödinger equation  $i\partial\Psi/\partial t = H\Psi$ . It follows from the given wave function that the probability  $\lim_{t \rightarrow \infty} |\langle \Psi | \Psi_2 \rangle|^2$  of excitation transfer, like the probability of resonance charge transfer,<sup>[11]</sup> is given by

$$W = \sin^2 \int_{-\infty}^{+\infty} \frac{(E_u - E_g)}{2} dt.$$

Since  $E_u - E_g$  depends exponentially on the interatomic distance, the cross section  $\sigma_{tr}$  for excitation transfer is given by a formula that is analogous to the case of resonant charge transfer:<sup>[10]</sup>  $\sigma_{tr} = \pi R_0^2/2$ , where  $R_0$  is the impact parameter for which

$$\int_{-\infty}^{+\infty} \frac{|E_g - E_u|}{2} dt = 0.28. \quad (15a)$$

Equation (15a) is valid for s-state excited electrons, and can be converted to

$$\sqrt{\pi R_0/2\beta} |E_g - E_u|(R_0) = 0.28 v. \quad (15b)$$

The diffusion coefficient of metastable atoms is defined like the diffusion coefficient of ions in their own gas. First, the dependence of the cross section for excitation transfer on the collisional velocity is the same, [ $\sim \ln^2(c/v)$ ], as that of the cross section for resonant charge transfer. Secondly, as a result of excitation transfer an excited atom is scattered at an angle  $\chi = \pi$  in the c.m. system (neglecting atomic elastic scattering). Therefore the diffusion cross section  $\sigma^*$  for scattering of a metastable atom in its own gas is, just as in the case of resonance charge transfer,<sup>[11]</sup>

$$\sigma^* = \int (1 - \cos \chi) d\sigma_{tr} = 2\sigma_{tr}.$$

From the analogy with resonance charge transfer we obtain the diffusion coefficient  $D$  of metastable atoms in their own gas:<sup>[12]</sup>

$$D = \frac{3(\pi T)^{1/2}}{8NM^{1/2}}, \quad \bar{\sigma} = \frac{40}{41} \pi R_0^2 \left( 2.1 \sqrt{\frac{2T}{M}} \right), \quad (16)$$

where  $T$  is the gas temperature,  $N$  is the gas density,  $M$  is the mass of atomic nuclei, and  $R_0$  is the impact parameter determined from (16).

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Translated by I. Emin