Theoret. Chim. Acta (Berl.) 34, 73—77 (1974)

Electron Transfer in Atomic-Molecular Collisions

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Received August 13, 1973/January 14, 1974

Expressions for the interaction between covalent (A + B) and inonic ($A^- + B^+$) terms in their pseudo-crossing point are obtained. Illustrating calculations are done for the excitation of $K(^2S \to {}^2P)$ by N_2.

Key words: Atomic-molecular collisions – Pseudo-crossing point of covalent and ionic terms

1.

In collisions of atoms and molecules the probabilities of different processes with electron transfer are often determined by exchange interaction between ionic and covalent terms at their pseudo-crossing point [1]. Examples are charge transfer between negative and positive ions [1] and vibrational transitions in the quenching of alkali metals by N_2 (see Refs. [2, 3] and the works cited there).

Consider the process

$$A^- + B^+ \to A + B \qquad (1)$$

Let the action range ϱ of the effective interaction V_A between the active electron and the particle A is small compared with the interatomic distance R. Here two cases are possible. a) A^- is a stable ion with electron affinity $E_a = \alpha^2/2$[1]. Then pseudo-crossing of terms takes place at $R_0 \simeq R_a = (I_B - E_a)^{-1}$ (I_B is the ionization potential of B and we assume that $I_B > E_a$), that is A is in the classically forbidden region for the valence electron of B. b) A^- is a quasistationary state with corresponding resonance energy $E_n = k_n^2/2$. Under the influence of the ion B^+ this ionic state becomes stable (when $R < E_a^{-1}$) and when $R_0 \simeq R_n = (I_B + E_n)^{-1}$ (i.e. A is in the inner region of B) pseudo-crossing of covalent and ionic terms takes place.

The first case was considered in the works [4–6]. In Ref. [4] δ-representation for V_A was used and by means of Coulomb Green's function the level splitting of hydrogen atom at large distances ($R_0 \gg I_B^{-1}, E_a^{-1}$) was investigated. The result of Ref. [5] is valid only if $m = 0$ and $(I_B - E_a)/I_B \ll 1$. The result of Ref. [6] is not correct (e.g. the coefficient C_0 in [6] tends to infinity at the crossing point). Some particular situations belonging to the second case were studied in Refs. [2, 3, 7, 8].

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[1] Unless otherwise specified, atomic units are used.

2.

In Ref. [9] the general formula for the splitting ΔE of adiabatic terms at the pseudo-crossing point has been obtained

$$\Delta E \simeq 2\,\Delta U/(1-|S_{\mathrm{AB}}|^2) \tag{2}$$

$$\Delta U = \tfrac{1}{2}\left|\oint_{S_\varrho} (\psi_{\mathrm{B}}^* \nabla\psi_{\mathrm{A}} - \psi_{\mathrm{A}}^* \nabla\psi_{\mathrm{B}})\, ds\right| \tag{3}$$

where S_ϱ is the spere surface (in the coordinate space of the active electron) of the radius ϱ around the atom A, ψ_{A} and ψ_{B} are unperturbed electronic wave functions, S_{AB} is their overlap integral.

Consider first the one-electron approximation. Then $\psi_{\mathrm{B}} = \chi_{\mathrm{B}}(r')\, Y_{LM}^{\mathrm{B}}$, $\psi_{\mathrm{A}} = \chi_{\mathrm{A}}(r)\, Y_{\tilde{L}\tilde{M}}^{\mathrm{A}}$, where χ_{B} is the radial function of the valence electron with distance r' from B, χ_{A} is the radial function of the ion A^-, Y_{LM}^{B} and $Y_{\tilde{L}\tilde{M}}^{\mathrm{A}}$ are the corresponding spherical harmonics (the quantization is referred to interatomic axis AB). When $r \geqq \varrho$ in the first case we have

$$\chi_{\mathrm{A}} = \frac{C}{r}\, k_{\tilde{L}}(\alpha r) \tag{4}$$

$$\chi_{\mathrm{B}} = \chi_{\mathrm{B}}(R_a) \exp(\beta r \cos\theta) \tag{5}$$

and in the second case we have

$$\chi_{\mathrm{A}} = \sqrt{\frac{\Gamma_n}{k_n}}\, r^{-1} [\sin\delta_{\tilde{L}}^0\, j_{\tilde{L}}(k_n r) + \cos\delta_{\tilde{L}}^0\, n_{\tilde{L}}(k_n r)] \tag{6}$$

$$\chi_{\mathrm{B}} = \chi_0 \cos(k \cdot r \cdot \cos\theta) + \chi_1 \sin(k \cdot r \cdot \cos\theta) \tag{7}$$

where C is the constant which determines the asymptotic behaviour of χ_{A}, Γ_n is the width of quasi-stationary state, j_l, n_l, k_l and further i_l are modified spherical Bessel functions multiplied by their arguments, r and θ are the coordinates of the electron of with respect to A, δ_l^0 is the "potential" scattering phase, $\chi_0 = \chi_{\mathrm{B}}(R_n)$, $\chi_1 = k^{-1} \dfrac{\partial \chi_{\mathrm{B}}(R_n)}{\partial r'}$. In the quasiclassical approximation $\beta^2/2 = I_{\mathrm{B}} - R_a^{-1}$, $k^2/2 = R_n^{-1} - I_{\mathrm{B}}$ and β coincides with α and k coincides with k_n. The expression (6) corresponds to the normalization of χ_{A} to unity in the action region of V_{A} [10].

When calculating ΔU it is convenient to transfer the functions of B to the new center A. This transformation is given by the formula (8) below which is not difficult to obtain using the properties of spherical functions [11, 12]

$$\begin{aligned}
&\cos(k \cdot r \cdot \cos\theta)\, P_L^M(\mathrm{B}) \simeq Q_{LM} \sum_{l=0}^{\infty} (-1)^l (4l+2M+1)\, P_{2l+M}^M(\mathrm{A})\, j_{2l+M}(kr),\\
&\sin(k \cdot r \cdot \cos\theta)\, P_L^M(\mathrm{B}) \simeq Q_{LM} \sum_{l=0}^{\infty} (-1)^l (4l+2M+3)\, P_{2l+M+1}^M(\mathrm{A})\, j_{2l+M+1}(kr)
\end{aligned} \tag{8}$$

where P_L^M is associated Legendre polynomial (here it is supposed that $M \geqq 0$), $Q_{LM} = (L+M)!\,[M!\,(L-M)!\,(2kR_0)^M\, kr]^{-1}$.

As a result we have

$$\Delta U = |J(\tilde{L}, L, M)|\, \delta_{\tilde{M}M} \tag{9}$$

where J does not change if $M \to -M$ and when $M \geqq 0$

$$J = \frac{\pi}{4} C\, \chi_{\mathrm{B}}(R_a)\, T(\tilde{L}, L, M) \tag{10}$$

for the first case and

$$J = \sqrt{\frac{\Gamma_n}{k_n}} \frac{\cos\delta_{\tilde{L}}^0}{2}\, T(\tilde{L}, L, M) \cdot \begin{cases} \chi_0\,, & \text{if} \quad L = M + 2n \\ \chi_1\,, & \text{if} \quad L = M + 2n + 1\,, \quad n = 0, 1, 2, \ldots \end{cases} \tag{11}$$

for the second case,

$$T(\tilde{L}, L, M) = \left[\frac{(2L+1)(2\tilde{L}+1)(L+M)!\,(\tilde{L}+M)!}{(L-M)!\,(\tilde{L}-M)!}\right]^{1/2} [M!(2\varkappa R_0)^M]^{-1}$$

and $\varkappa$ stands for α or k_n (depending on the case considered).

As it was noted above the first case was considered in Ref. [4] where δ-potential for V_{A} was used. This approximation is valid if (in our definitions) $\alpha\varrho \ll 1$ and $\tilde{L} = 0$. The first two terms of series of ΔU were obtained using $1/R_a$ as a small parameter and one can see an additional condition of the application of the method [4]: $(1-\beta_0)^2 (2\beta_0^3 R_a)^{-1} \ll 1$, $\beta_0 = (2I_{\mathrm{B}})^{1/2}$. The approach under consideration makes it possible to study the more general case and in the suppositions of Ref. [4] gives the exact expression for ΔU.

3.

Let the outer shells of B and A$^-$ contain several equivalent electrons with orbital quantum numbers l^{B} and l^-. Then for the construction of many-electron wave functions one should use the coefficients of fractional parentage (see e.g. Ref. [13]). If the states of the particles under discussion are described by the following quantum numbers – A: L^{A}, M_L^{A}, S^{A}, M_S^{A}; B: L^{B}, M_L^{B}, S^{B}, M_S^{B}; B$^+$: L^+, M_L^+, S^+, M_S^+; A$^-$: L^-, M_L^-, S^-, M_S^- then one can obtain

$$\Delta U = \left| W \begin{pmatrix} S^+ & 1/2 & S^{\mathrm{B}} \\ M_S^+ & \mu^B & M_S^{\mathrm{B}} \end{pmatrix} \begin{pmatrix} S^{\mathrm{A}} & 1/2 & S^- \\ M_S^{\mathrm{A}} & \mu^- & M_S^- \end{pmatrix} J(l^{\mathrm{B}}, l^-, m^{\mathrm{B}}) \right| \delta_{m^{\mathrm{B}}m^-}\, \delta_{\mu^{\mathrm{B}}\mu^-} \tag{12}$$

where

$$W = [(2L^{\mathrm{B}}+1)(2S^{\mathrm{B}}+1)(2L^-+1)(2S^-+1)]^{1/2}\, G_{S^+L^+}^{S^{\mathrm{B}}L^{\mathrm{B}}}\, G_{S^{\mathrm{A}}L^{\mathrm{A}}}^{S^-L^-}$$
$$\cdot \begin{pmatrix} L^+ & l^{\mathrm{B}} & L^{\mathrm{B}} \\ M_L^+ & m^{\mathrm{B}} & M_L^{\mathrm{B}} \end{pmatrix} \begin{pmatrix} L^{\mathrm{A}} & l^- & L^- \\ M_L^{\mathrm{A}} & m^- & M_L^- \end{pmatrix},$$

$m^{\mathrm{B}} = M_L^{\mathrm{B}} - M_L^+$, $\mu^{\mathrm{B}} = M_S^{\mathrm{B}} - M_S^+$, $m^- = M_L^- - M_L^{\mathrm{A}}$, $\mu^- = M_S^- - M_S^{\mathrm{A}}$, $G_{SL}^{\tilde{S}\tilde{L}}$ is the corresponding coefficient of fractional parentage, $\begin{pmatrix} \cdots \\ \cdots \end{pmatrix}$ is the $3j$-symbol.

In the case when spin-orbital interaction can be neglected, total spin and its z-component (S^c, M_S^c for the state A+B and S^i, M_S^i for the state A$^-$+B$^+$) may be considered good quantum numbers for the quasi-molecule AB. Then

$$\Delta U = \left| W \begin{Bmatrix} S^{+} & 1/2 & S^{\mathrm{B}} \\ S^{\mathrm{A}} & S^{c} & S^{-} \end{Bmatrix} J(l^{\mathrm{B}}, l^{-}, m^{\mathrm{B}}) \right| \delta_{m\mathrm{B}m^{-}} \delta_{S^{c}S^{i}} \delta_{M_S^{c} M_S^{i}} \tag{13}$$

where $\begin{Bmatrix} \cdots \\ \cdots \end{Bmatrix}$ is the 6*j*-symbol.

It should be noted that if the quantization of the orbital momentum of A^{-} is referred not to the axis AB but to some other axis $\boldsymbol{n}$ (where ϑ is the angle berween the axes) then Kroneker symbols $\delta_{\tilde{M}M}$ and $\delta_{m^{\mathrm{B}}m^{-}}$ in (9, 12, 13) should be replaced by the absolute values of the rotational matrix elements $|D^{(\tilde{L})}_{\tilde{M}M}(\vartheta)|$ and $|D^{(l^{-})}_{m^{\mathrm{B}}m^{-}}(\vartheta)|$ (the expressions for them are given in Ref. [14]).

4.

In particular the excitation of $\mathrm{K}(^{2}S \rightarrow {}^{2}P)$ by N_2 is now considered. Experimental study of the scattering of slow electrons by N_2 [15] has shown the existance of quasistationary N_2^{-} states. A mechanism of N_2^{-} formation has been investigated in theoretical [16, 17] and experimental [18] works. It has been shown that the N_2^{-} ion is formed in the $^{2}\Pi_g$ electronic state and that this quasi-stationary state is ensured by a centrifugal barrier with $\tilde{L}=2$. The dynamics of the K–N_2 collision have been investigated in Refs. [2, 3]. For the excitation cross section σ_e one can obtain the following expression

$$\sigma_e(E) = \frac{\pi R_s^2}{E} \int_{E_0}^{E} P_e(E_r)\, dE_r \tag{14}$$

where E is the relative kinetic energy, R_s is the pseudo-crossing point of covalent (^{2}S) and ionic terms, E_0 is the threshold energy which is equal to the excitation

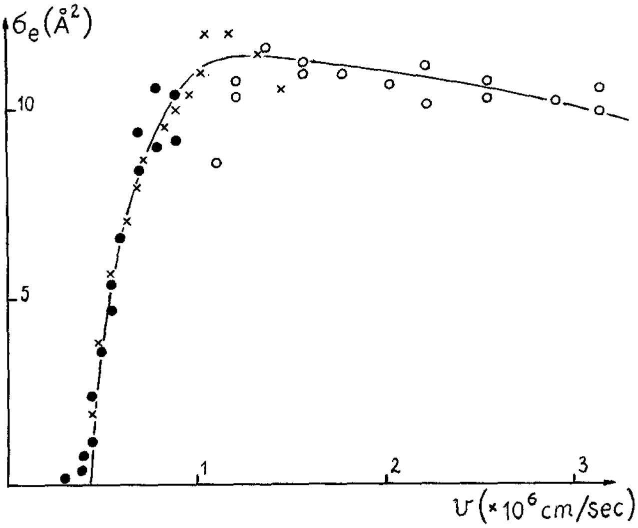

Fig. 1. Cross sections for excitation of K by N_2 as a function of relative velocity. Theory: ——; experiment: ○ Ref. [21], ● Ref. [22], × Ref. [23]. Measurements are normalised to absolute calculations

energy of K, P_e is the excitation probability, E_r is the radial kinetic energy at the pseudo-crossing point. For this calculation we use $\Gamma_n = 0.2$ eV, the wave function as given in Ref. [19], $\delta_2^0 \simeq \pi \cdot p \cdot k_n^2/105$ [20] where p is the polarizability of N_2. Then we obtain for the interaction between different covalent and ionic states (see Ref. [3]): $|\Delta U_s|^2 \simeq 4_{10^{-4}} \cos^2 \vartheta \sin^2 \vartheta$, $|\Delta U_0|^2 \simeq 5.7_{10^{-4}} \cos^2 \vartheta \sin^2 \vartheta$, $|\Delta U_1^+|^2 \simeq 0.34_{10^{-4}} (1 - 2\cos^2 \vartheta)^2$, $|\Delta U_1^-|^2 \simeq 0.34_{10^{-4}} \cos^2 \vartheta$ and $R_s = 5.7, R_1 = 6.8, R_0 = 7.5$, R_1 and R_0 are the pseudo-crossing points of final covalent ($^2\Pi$ and $^2\Sigma$) and ionic terms. In Fig. 1 the calculated σ_e is compared with the experimental data from Refs. [21–23] where σ_e has been measured in relative units.

It is to be emphasized that the possibility of the intermediate inonic state formation should be taken into account when considering the collisions of atoms with the weakly bound electrons with molecules which are able to form temporary negative ions (e.g. H_2, N_2, CO [18]).

In conclusion the author expresses his gratitude to Prof. E. E. Nikitin for the discussion of this work.

References

1. Bates, D., in: Atomic and molecular processes. New York and London: Academic Press 1962
2. Andreev, E. A.: Dissertation, MFTI. Moscow 1971 (in Russian)
3. Andreev, E. A.: Thermophys. High Temp. **10**, 708 (1972) (in Russian)
4. Komarov, I. V.: Dissertation, LGU. Leningrad 1968 (in Russian)
5. Smirnov, B. M.: Dokl. Akad. Nauk. SSSR **161**, 92 (1965) (in Russian)
6. Janev, R. K., Salin, A.: J. Phys. B **5**, 177 (1972)
7. Bjerre, A.: Theoret. Eksptl. Chem. **4**, 583 (1968) (in Russian)
8. Andreev, E. A., Voronin, A. I.: Chem. Phys. Letters **3**, 188 (1968)
9. Andreev, E. A.: Theoret. Chjm. Acta (Berl.) **30**, 191 (1973)
10. Baz, A. I., Zeldovitch, Ja. B., Perelomov, A. M.: Scattering, reations and decays in nonrelativistic quantum mechanics. Moscow: Fizmatgiz 1966 (in Russian)
11. Gradshtein, I. S., Ryzhik, I. M.: Tables of integrals, sums, series and products. Moscow: Fizmatgiz 1963 (in Russian)
12. Davidovič, D. M., Janev, R. K.: Phys. Rev. **186**, 89 (1969)
13. Sobelman, I. I.: Introduction to the theory of the atomic spectra. Moscow: Fizmatgiz 1963 (in Russian)
14. Edmonds, A. R.: Angular momentum in quantum mechanics. Princeton: Princeton University Press 1957
15. Schulz, G. L.: Phys. Rev. A **135**, 988 (1964)
16. Bardsley, J. N., Mandl, F., Wood, A. R.: Chem. Phys. Letters **1**, 359 (1967)
17. Krauss, M., Mies, F. H.: Phys. Rev. A **1**, 1592 (1970)
18. Erhard, H., Langhans, L., Linder, F., Tailor, H. S.: Phys. Rev. **173**, 222 (1968)
19. Gombas, P.: Pseudopotentiale. New York: Springer-Verlag 1967
20. O'Malley, T. F., Spruch, L., Rosenberg, T. J.: J. Math. Phys. **2**, 491 (1961)
21. Anderson, R. W., Aquilanti, V., Herschbach, D. R.: Chem. Phys. Letters **4**, 5 (1969)
22. Kempter, V., Wecklenbrauck, W., Mensinger, M., Schuller, G., Herschbach, D. R., Schlier, Ch.: Chem. Phys. Letters **6**, 97 (1970)
23. Lacmann, K., Herschbach, D. R.: Chem. Phys. Letters **6**, 106 (1970)

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