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ELECTRON TERMS IN THE FIELD OF TWO DIFFERENT COULOMB CENTERS

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It is demonstrated that the Neumann-Wigner theorem on the impossibility of intersection of terms of the same symmetry is not valid for electrons in the field of two Coulomb centers. Terms for large and small distances between the nuclei are compared for the case when the nuclear charges are different. It is indicated that term intersections exist which are important for charge-exchange processes during collisions between hydrogen atoms and nuclei.

INTRODUCTION

We consider a negatively charged particle located in the field of two stationary Coulomb centers with charges Z_1 and Z_2. In the case when $Z_1 = Z_2$, this system represents essentially a molecular hydrogen ion, whose wave functions and energy terms have been thoroughly investigated.[1-4] It is interesting to examine the case $Z_1 \neq Z_2$. Systems of this kind arise, for example, when the hydrogen mesic atom ($Z_1 = 1$) approaches nuclei of other elements ($Z_2 > 1$)† or when multiply-charged ions such as He^{++}, Li^{+++} etc. pass through hydrogen.

Schrödinger's equation for the problem of two Coulomb centers (in atomic units $e = 1$, $\hbar = 1$, $m = 1$) has the form

$$-\frac{1}{2}\Delta\Psi + \left(-\frac{Z_1}{r_1} - \frac{Z_2}{r_2} + \frac{Z_1Z_2}{R}\right)\Psi = E\Psi, \qquad (1)$$

where R is the distance between nuclei, and r_1 and r_2 are the distances from the electron to the first and second nuclei, respectively. Introducing the elliptic coordinates

$$\xi = (r_1 + r_2)/R, \qquad \eta = (r_1 - r_2)/R, \qquad \varphi = \operatorname{arctg}(y/x), \qquad (2)‡$$

we can separate the variables in Eq. (1). Putting

$$\Psi = X(\xi)Y(\eta)e^{im\varphi}, \qquad (3)$$

we obtain the following equations for the functions $X(\xi)$ and $Y(\eta)$:

$$\frac{d}{d\xi}\left[(\xi^2 - 1)\frac{dX}{d\xi}\right] + \left(-\frac{m^2}{\xi^2 - 1} + R(Z_1 + Z_2)\xi - p^2\xi^2 + A\right)X = 0, \qquad (4a)$$

$$\frac{d}{d\eta}\left[(1 - \eta^2)\frac{dY}{d\eta}\right] + \left(-\frac{m^2}{1 - \eta^2} + R(Z_2 - Z_1)\eta + p^2\eta^2 - A\right)Y = 0, \qquad (4b)$$

$$p^2 = -R^2W/2, \quad W = E - Z_1Z_2/R, \qquad (5)$$

The quantity A is the separation constant.

To determine the eigenvalues of (1) it is customary to find the separation constant A from Eqs. (4a) and (4b) respectively as a function of the parameters p and R. Let $A = A_{n\xi}(R, p, m)$ and $A = A_{n\eta}(R, p, m)$ be the eigenvalues of the separation constant, determined from (4a) and (4b) subject to the condition that $X(\xi)$ be finite at $\xi = 1$ and $\xi = \infty$, and $Y(\eta)$ be finite at $\eta = \pm 1$ (n_ξ and n_η are the numbers of the eigenvalues). Then the equality

$$A_{n_\xi}(R, p, m) = A_{n_\eta}(R, p, m) \qquad (6)$$

enables us to determine the function $p = p_{n\xi,n\eta,m}(R)$ and, consequently, the molecular terms

$$E = E_{n_\xi, n_\eta, m}(R).$$

It is obvious that as $R \to \infty$ the energy of the terms should be expressed through the quantum numbers of the hydrogen-like atoms with charge Z_1 and Z_2, whereas the molecular terms should go, as $R \to 0$, into the energy levels of the compound atom with nuclear charge $Z_1 + Z_2$.

The purpose of the present work is a comparison of the molecular terms at large and small

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†Being electrically neutral, hydrogen mesic atoms pass practically freely through the electron shells of the atoms. Interaction processes between hydrogen mesic atoms and other nuclei (particularly charge exchange) are due to the smallness of the mesic-atomic orbits at the distances where the effect of the electron shell of the atom on the interaction can be neglected.

‡arctg = tan^{-1}.

distances between nuclei, i.e., the determination of the level of the combined atom into which the level of the individual atom (with charge Z_1 or Z_2) goes as the distance between nuclei decreases from $R = \infty$ to $R = 0$. At first glance it may appear that such a comparison is easy to obtain from the well-known Neumann-Wigner theorem on the impossibility of intersection of terms of the same symmetry.[5] However, as will be shown in the next section, the single-electron molecule under consideration is an exceptional case, for which the Neumann-Wigner theorem is not satisfied. The terms will therefore be compared by calculating the number of zeros of the functions $X(\xi)$ and $Y(\eta)$ at large and small distances between nuclei respectively, as is done for H_2^+ in Bethe's book.[6] We have established at the same time that intersections of molecular terms do exist, a very important factor in charge-exchange processes in atomic collisions.

POSSIBILITY OF INTERSECTION OF TERMS OF THE SAME SYMMETRY

The well known statement of Neumann and Wigner, that terms of the same symmetry cannot intersect in the case of diatomic molecules, is based on the following considerations (see, for example, reference 7). Assume that at a certain distance R_0 between the nuclei the Hamiltonian $\hat{H}(R_0)$ has nearly equal eigenvalues E_1^0 and E_2^0, corresponding to eigenfunctions ψ_1^0 and ψ_2^0. Writing for the Hamiltonian $\hat{H}(R)$ at R close to R_0

$$\hat{H}(R) = \hat{H}(R_0) + (\delta\hat{H} / \delta R_0 \delta R = \hat{H}(R_0) + \hat{V}, \tag{7}$$

we can readily show that the difference between the eigenvalues of the energy at the point R is

$$\{[(E_1^0 + V_{11}) - (E_2^0 + V_{22})]^2 + 4V_{12}^2\}^{1/2}, \tag{8}$$

where V_{ik} are the matrix elements of the operator $\hat{V} = (\delta\hat{H}/\delta R)_0 \delta R$, taken over the wave functions ψ_1^0 and ψ_2^0.

For the terms to intersect it is necessary that both members under the square root in Eq. (8) vanish simultaneously. It is usually assumed that this condition can be satisfied only for terms of different symmetry, when $V_{12} \equiv 0$. On the other hand, in the case of terms of the same symmetry we have $V_{12} \not\equiv 0$ and simultaneous vanishing of both members of the equation is generally impossible, since they are functions of only one parameter δR.

We shall show later on that a diatomic molecule with one electron is an exceptional case, when simultaneous vanishing of both members in expression (8) for terms of the same symmetry, and hence intersection of terms of the same symmetry is possible. Writing down the Hamiltonian of the system in elliptical coordinates

$$\hat{H} = -\frac{2}{R^2(\xi^2-\eta^2)}\left\{\frac{\partial}{\partial\xi}(\xi^2-1)\frac{\partial}{\partial\xi} + \frac{\partial}{\partial\eta}(1-\eta^2)\frac{\partial}{\partial\eta} + \frac{\xi^2-\eta^2}{(\xi^2-1)(1-\eta^2)}\frac{\partial^2}{\partial\varphi^2}\right\} - \frac{2Z_1}{R(\xi-\eta)} - \frac{2Z_2}{R(\xi+\eta)} + \frac{Z_1Z_2}{R}, \tag{9}$$

we obtain from the operator $\hat{V}$ an expression which can be represented as

$$\hat{V} = \frac{\delta\hat{H}}{\delta R}\delta R = \left\{-\frac{2}{R}\hat{H} + \frac{Z_1Z_2}{R^2} - \frac{1}{R}\left(\frac{Z_1}{r_1} + \frac{Z_2}{r_2}\right)\right\}\delta R. \tag{10}$$

Calculation of the matrix element V_{12} shows that the integrals of the first two constituents vanish because of the orthogonality of the functions ψ_1^0 and ψ_2^0, and we therefore obtain

$$V_{12} = -\frac{\delta R}{R}\int\left(\frac{Z_1}{r_1} + \frac{Z_2}{r_2}\right)d\tau. \tag{11}$$

Let us examine the matrix element of $1/r_1$ for functions of the same symmetry (the same m). Substituting ψ_1^0 and ψ_2^0 as given by (3) we obtain

$$\left\langle\frac{1}{r_1}\right\rangle_{12} = \frac{\pi R^2}{2}\left\{\int_1^\infty X_1\xi X_2\,d\xi\int_{-1}^{+1} Y_1Y_2\,d\eta - \int_1^\infty X_1X_2\,d\xi\int_{-1}^{+1} Y_1\eta Y_2\,d\eta\right\}. \tag{12}$$

On the other hand, it follows from Eqs. (4a) and (4b) for the functions X_1, X_2, and Y_1, Y_2, that

$$(A_1 - A_2)\int_1^\infty X_1X_2\,d\xi = (p_1^2 - p_2^2)\int_1^\infty X_1\xi^2X_2\,d\xi,$$

$$(A_1 - A_2)\int_{-1}^{+1} Y_1Y_2\,d\eta = (p_1^2 - p_2^2)\int_{-1}^{+1} Y_1\eta^2Y_2\,d\eta. \tag{13}$$

The separation constant A can be regarded as the eigenvalue of the corresponding operators in (4a) and (4b) for given p and R. Inasmuch as the eigenvalue spectrum is nondegenerate for the one-dimensional equation, we have $A_1 \neq A_2$ (if $\psi_1^0 \not\equiv \psi_2^0$ and $R \neq 0$) and consequently, taking (5) and (13) into account, we can represent $\langle r_1^{-1}\rangle_{12}$ in the form

$$\left\langle\frac{1}{r}\right\rangle_{12} = \frac{\pi R^4}{4}\frac{(E_1^0 - E_2^0)}{(A_1 - A_2)}\{\langle\xi^2\rangle_{12}\langle\eta\rangle_{12} - \langle\xi\rangle_{12}\langle\eta^2\rangle_{12}\}. \tag{14}$$

An analogous argument for $\langle r_2^{-1}\rangle_{12}$ yields

$$V_{12} = \text{const}\cdot(E_1^0 - E_2^0)\delta R. \tag{15}$$

Thus, in the approximation considered here V_{12} vanishes simultaneously with $E_1^0 - E_2^0$, and consequently terms of the same symmetry can intersect.

That in the H_2^+ molecule the terms of the same symmetry actually intersect has been known for a long time (see, for example, reference 6, Fig. 52), but the connection between this result and the general Neumann-Wigner theorem has never been discussed (as far as the authors know). The foregoing analysis shows that the intersection of terms of the same symmetry in the two-center problem is in some sense "accidental." The intersection takes place only for an exact Coulomb interaction which leads to the separation of variables in (4); any perturbation that disturbs the possibility of separation of variables (for example, allowance for the finite dimensions of the nuclei) causes the terms to move appart.

COMPARISON OF TERMS FOR LARGE AND SMALL DISTANCES

The number of roots of the functions $X(\xi)$ and $Y(\eta)$ in the intervals $1 < \xi < \infty$ and $-1 < \eta < 1$ cannot vary with the parameter R.* This fact can be used to compare terms for large and small distances between nuclei. Let n_ξ be the number of zeros of the function $X(\xi)$ $(1 < \xi < \infty)$, and let n_η be the number of zeros $Y(\eta)$ $(-1 < \eta < +1)$. Then, recognizing that as $R \to 0$ Eq. (4a) changes into the equation for the radial function of a hydrogen-like atom with nucleus $Z_1 + Z_2$, and Eq. (4b) changes into the equation for the associated Legendre polynomials, it is easy to express the quantum numbers of the compound atom through n_ξ and n_η.

As $R \to 0$

$$n_r = n_\xi, \qquad l - |m| = n_\eta, \tag{16}$$

where l is the orbital momentum and n_r is the radial quantum number of the combined atom. The principle quantum number of the compound atom N is expressed through n_ξ, n_η, and m with the aid of the equation

$$N = n_r + l + 1 = n_\xi + n_\eta + |m| + 1. \tag{17}$$

As $R \to \infty$, the elliptical coordinates go into parabolic coordinates, and the equations in (4) go into equations for the hydrogen-like atom Z_1 (or Z_2) in parabolic coordinates. In order to compare terms at larger and smaller distances, it is necessary to express n_ξ and n_η through the parabolic quantum numbers of the separated atoms. Such an expression is quite easy to derive for n_ξ. Introducing the variable

$$\nu = (\xi - 1)R, \qquad 0 \leqslant \nu < \infty, \tag{18}$$

we obtain from (4a) an equation which has the following form when $\nu \ll R$ $(R \gg 1)$

$$\nu X'' + X' + \left[-\frac{m^2}{4\nu} - \frac{p^2}{R^2}\nu + \frac{A - p^2 + R(Z_1 + Z_2)}{2R}\right] X = 0. \tag{19}$$

A solution of (19), finite at $\nu = 0$, is the function

$$X = \nu^{|m|/2} e^{-p\nu/R} F \times \left(\frac{|m|+1}{2} - \frac{A - p^2 + R(Z_1 + Z_2)}{4p};\ |m| + 1;\ \frac{2p}{R}\nu\right) \tag{20}$$

[$F(\alpha; \gamma; x)$ is the confluent hypergeometric function].

In order for the solution (20) to remain bounded with increasing ν, it is necessary that the first argument of the confluent hypergeometric function be equal to a negative integer $(-n_1)$. The separation constant is consequently

$$A = A_\xi = p^2 - R(Z_1 + Z_2) + 2p(2n_1 + |m| + 1), \tag{21}$$

and the number of positive roots of the function (20) is n_1. Thus

$$n_\xi = n_1, \tag{22}$$

where n_1 is the parabolic quantum number. (We note that for large R $\nu \approx r_1 - z_1$ near the first nucleus and $\nu = r_2 + z_2$ near the second one; the z axis is assumed to join the first nucleus to the second.)

Let us find now an expression for n_η. To be specific, we assume that the electron remains at the nucleus Z_1 after the nuclei have separated. Introducing a new variable μ:

$$\mu = R(1 + \eta), \qquad 0 \leqslant \mu \leqslant 2R, \tag{23}$$

we obtain in the region $\mu \ll R$ $(R \gg 1)$ the following equations for $Y(\mu)$:

$$\mu Y'' + Y' + \left\{-\frac{m^2}{4\mu} - \frac{p^2}{R^2}\mu + \frac{-A + p^2 - R(Z_2 - Z_1)}{2R}\right\} Y = 0. \tag{24}$$

A solution of (24), finite when $\mu = 0$ and exponentially decreasing when $\mu \gg 1$ (the electron is assumed to be at the nucleus Z_1!), is the function

$$Y(\mu) = \mu^{|m|/2} e^{-p\mu/R} F(-n_2;\ |m| + 1;\ 2p\mu/R), \tag{25}$$

where n_2 is a positive integer. The separation constant now has the form

$$A = A_\eta = p^2 - 2p(2n_2 + |m| + 1) - R(Z_2 - Z_1). \tag{26}$$

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*Actually, were the number of roots inside the indicated intervals to increase or decrease with changing R, this would mean that a multiple root ξ_0 (or η_0) exists for some $R = R_0$, i.e., $X(\xi_0) = X'(\xi_0) = 0$ [or $Y(\eta_0) = Y'(\eta_0) = 0$]. By virtue of (4), this should lead to $X(\xi) \equiv 0$ [or $Y(\eta) \equiv 0$].

Equating (21) and (26) we obtain for the electron energy

$$W = -2p^2/R^2 = -Z_1^2/2n^2, \qquad n = n_1 + n_2 + |m| + 1, \tag{27}$$

i.e., the energy of an isolated atom with nucleus Z_1. The wave function (3), in which $X(\xi)$ and $Y(\eta)$ are specified by (20) and (25) respectively, is the wave function of the isolated atom Z_1 in parabolic coordinates.

The members of higher order in 1/R can be obtained by expanding the solutions (4a) and (4b) in Laguerre polynomials. Inclusion of the next two terms in the series gives for the separation constant

$$\begin{aligned} A = A_\xi = p^2 &+ \{2p(2n_1 + |m| + 1) - R(Z_1 + Z_2)\} \\ &+ \{(2n_1 + 1)(n_1 + |m| + 1) \\ &- n_1 - (Z_1 + Z_2)(2n_1 + |m| + 1) R/2p\} \\ &- (R^2/16p^3)\{(Z_1 + Z_2)^2 (2n_1 + |m| + 1) \\ &- (Z_1 + Z_2)(2p/R)[(2n_1 + |m| + 1)(2n_1 + |m| + 2) \\ &+ 2n_1(n_1 + |m|)] \\ &+ (4p^2/R^2)(2n_1 + |m| + 1)[(n_1 + 1)(n_1 + |m| + 1) \\ &+ n_1(n_1 + |m|)]\}; \end{aligned} \tag{28}$$

$$\begin{aligned} A = A_\eta = p^2 &- \{2p(2n_2 + |m| + 1) + R(Z_2 - Z_1)\} \\ &+ \{(2n_2 + 1)(n_2 + |m| + 1) - n_2 \\ &+ (Z_2 - Z_1)(2n_2 + |m| + 1) R/2p\} \\ &+ (R^2/16p^3)\{(Z_2 - Z_1)^2 (2n_2 + |m| + 1) \\ &+ (Z_2 - Z_1)(2p/R)[(2n_2 \\ &+ |m| + 1)(2n_2 + |m| + 2) + 2n_2(n_2 + |m|)] \\ &+ (4p^2/R^2)(2n_2 + |m| + 1)[(n_2 + 1)(n_2 + |m| + 1) \\ &+ n_2(n_2 + |m|)]\}. \end{aligned} \tag{29}$$

Equating (28) and (29) we obtain, as expected, for the atom Z_1 in the field of the nucleus Z_2,

$$W = -Z_1^2/2n^2 - Z_2/R + \tfrac{3}{2}(n_1 - n_2)\, nZ_2/Z_1R^2. \tag{30}$$

The function (25) has n_2 roots located at a finite distance from the nucleus Z_1. In the case when $Z_1 = Z_2$, owing to the symmetry of the Hamiltonian with respect to reflection at the center of the molecule [invariance of (4b) under a substitution of $-\eta$ for η], the solution of (4b) should have near Z_2 a form analogous to (25) (with the sign of η reversed). It is therefore possible to express n_η directly in terms of n_2: $n_\eta = 2n_2$ for symmetrical terms and $n_\eta = 2n_2 + 1$ for antisymmetrical ones (see reference 6).

When $Z_1 \neq Z_2$ the determination of the number of zeros n_η is a more complicated matter and calls for an investigation of the behavior of the function $Y(\eta)$ near the second nucleus $\eta \approx 1$). Introducing the variable

$$\mu_1 = R(1 - \eta), \qquad 0 \leqslant \mu_1 \leqslant 2R, \tag{31}$$

we can write (4b) near $\mu_1 \ll R$ in the form

$$\mu_1 Y'' + Y' + \left\{ -\frac{m^2}{2\mu_1} - \frac{p^2}{R^2}\mu_1 + \frac{-A + p^2 + R(Z_2 - Z_1)}{2R} \right\} Y = 0, \tag{32}$$

where the constants A and p/R are determined by the conditions (21) and (26).

A solution of (32), finite when $\mu_1 = 0$ (apart from a constant factor), is

$$Y = \mu_1^{|m|/2} e^{-p\mu_1/R} F(\alpha;\, |m| + 1;\, 2p\mu_1/R), \tag{33}$$

where

$$\alpha = -n_2 - n(Z_2 - Z_1)/Z_1. \tag{34}$$

Depending on the magnitude and the sign of α, three different possibilities may occur: (1) $\alpha > 0$, (2) $\alpha < 0$ and Z_2n/Z_1 not an integer, (3) $\alpha < 0$ and $Z_2n/Z_1 = n'$ an integer. Let us consider each of these cases.

(1) The condition $\alpha > 0$ is possible only when $Z_1 > Z_2$ and n_2 are sufficiently small

$$0 \leqslant n_2 < n(Z_1 - Z_2)/Z_1. \tag{35}$$

In this case the solution (33) increases exponentially with increasing μ_1 ($1 \ll \mu_1 \ll R$). Thus the wave function of the electron near the nucleus Z_2 cannot be represented in the form of the wave function of a hydrogen-like atom with nucleus Z_2, and is merely the function of a hydrogen atom with nucleus Z_1, but distorted in the vicinity of the nucleus Z_2. Inasmuch as the confluent hypergeometric function $F(\alpha;\, |m| + 1;\, 2p\mu_1/R)$ has no positive roots when $\alpha > 0$, it is clear that the zeros of the function $Y(\eta)$ are all located near the nucleus Z_1 and according to (25)

$$n_\eta = n_2. \tag{36}$$

(2) If $\alpha < 0$ and Z_2n/Z_1 is not an integer, then the investigated level (as $R \to \infty$) of the atom Z_1 [see (27)] coincides with none of the levels of the atom Z_2. Therefore, as in case (1), the wave function of the electron near Z_2 is essentially the wave function of an atom with nucleus Z_1, distorted by the field of Z_2. At large distances between the nuclei, the Coulomb field of Z_2 hardly changes the wave function of the electron near Z_1 [see (25)], whereas its influence in the vicinity of Z_2 itself is large. When $\alpha < 0$ oscillations of the wave function occur near Z_2 (see Fig. 1). Considering that for non-integral α ($\alpha < 0$) the number of zeros of the confluent hypergeometric function $F(\alpha;\, |m| + 1;\, 2p\mu_1/R)$ is equal to $\{\mathrm{Ent}(-\alpha) + 1)\}$ (where $\mathrm{Ent}(x)$ is the integral part of x), we can determine n_η from (25), (33), and (34);

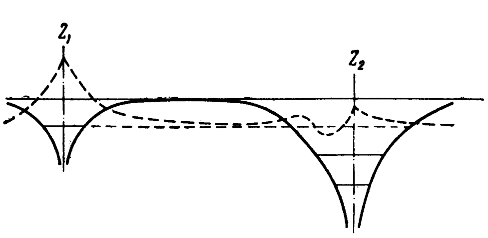

FIG. 1

$$n_\eta = n_2 + 1 + \mathrm{Ent}\,[n_2 + n\,(Z_2 - Z_1)/Z_1]. \tag{37}$$

(3) If $\alpha < 0$ and $Z_2 n/Z_1 = n'$, where n' is an integer, then the level of the atom Z_1 (27) coincides with that level of the atom Z_2, whose principal quantum number is n'. From (20), (33), and (34) we see that the wave function of the electron near Z_2 is the wave function of a hydrogen-like atom with parabolic quantum numbers $n_1' = n_1$ and $n_2' = n' - n_1 - |m| - 1$. In this case therefore, as $R \to \infty$, degeneracy takes place and the regular wave functions have the form (3), where $X(\xi)$ is given by (20) and $Y(\eta)$ is a linear combination of (25) and (33). Taking into account the fact that an additional root appears for one of the linear combinations of (25) and (33) in the interval $-1 < \eta < 1$, we obtain

$$n_\eta = n_2 + n_2' \tag{38a}$$

or

$$n_\eta = n_2 + n_2' + 1. \tag{38b}$$

It will be shown in the appendix that (38a) and (38b) hold when the electron is at the nucleus with the smaller or larger charge, respectively, as $R \to \infty$.

Using (16), (17), and (35) — (38), let us summarize the results obtained. Assume, specifically, that $Z_1 < Z_2$ and that (n_1, n_2, m) and (n_1', n_2', m) are the parabolic quantum numbers of the atoms Z_1 and Z_2 as $R \to \infty$. We then have:

A. If the electron is located (when $R = \infty$) at the nucleus $Z_1 (Z_1 < Z_2)$, then

$$l = \begin{cases} n_2 + |m| + 1 + \mathrm{Ent}\left(n_2 + n\dfrac{Z_2 - Z_1}{Z_1}\right), & \text{when } \dfrac{Z_2}{Z_1}\,n \neq \text{interger} \\ 2n_2 + |m| + n\,\dfrac{Z_2 - Z_1}{Z_1}, & \text{when } \dfrac{Z_2}{Z_1}\,n = \text{interger} \end{cases}, \tag{39}$$

$$N = \begin{cases} n + 1 + \mathrm{Ent}\left(n_2 + n\dfrac{Z_2 - Z_1}{Z_1}\right), & \text{when } \dfrac{Z_2}{Z_1}\,n \neq \text{interger} \\ n_2 + n\,\dfrac{Z_2}{Z_1}, & \text{when } \dfrac{Z_2}{Z_1}\,n = \text{interger} \end{cases} \tag{40}$$

B. If the electron is located (when $R = \infty$) at the nucleus $Z_2 (Z_2 > Z_1)$, then

$$l = \begin{cases} n_2' + |m|, & \text{when } n_2' \geqslant n'\,\dfrac{Z_2 - Z_1}{Z_2} \\ n_2' + |m| + 1 \\ \quad + \mathrm{Ent}\left(n_2' - n'\,\dfrac{Z_2 - Z_1}{Z_2}\right), & \text{when } n_2' < n'\,\dfrac{Z_2 - Z_1}{Z_2} \end{cases}, \tag{41}$$

$$N = \begin{cases} n', & \text{when } n_2' < n'\,\dfrac{Z_2 - Z_1}{Z_2} \\ n' + 1 + \mathrm{Ent}\left(n_2' - n'\,\dfrac{Z_2 - Z_1}{Z_2}\right), & \text{when } n_2' \geqslant n'\,\dfrac{Z_2 - Z_1}{Z_2} \end{cases} \tag{42}$$

Formulas (39) — (42) establish the connection between the terms of the isolated atoms (at $R = \infty$) and the terms of the combined atom ($R = 0$).

BEHAVIOR OF TERMS AT SMALL DISTANCES BETWEEN NUCLEI

The behavior of the terms when the distances between the nuclei are small can be explained by using as the zeroth approximation the states of a combined atom with charge $Z_1 + Z_2$, located in the center of charge of the nuclei Z_1 and Z_2. Regarding

$$U = -\left(\frac{Z_1}{r_1} + \frac{Z_2}{r_2}\right) + \frac{Z_1 + Z_2}{r} \tag{43}$$

as a perturbation, we can show (as is done for the case $Z_1 = Z_2$, see reference 5) that the regular functions of the zeroth approximation, with allowance for degeneracy, are the wave functions of the combined atom $Z_1 + Z_2$:*

$$\psi^0 = v_{N,l}(r)\,Y_{lm}(\vartheta, \varphi), \tag{44}$$

and that the energy of the terms is given (accurate to R^2) by the expression

$$W = -\frac{(Z_1 + Z_2)^2}{2N^2} - 2Z_1Z_2(Z_1 + Z_2)^2\,\frac{[l(l+1) - 3m^2]\,R^2}{N^3 l(l+1)(2l-1)(2l+1)(2l+3)}. \tag{45}$$

The sequence of the terms is the same as given by Bethe[6] for the case $Z_1 = Z_2$. (The energy of the s terms is obtained formally from (4b) by putting in it $m = 0$, canceling by l, and setting $l = 0$.)

TERM INTERSECTIONS CORRESPONDING TO CHARGE EXCHANGE

The behavior of the terms when the distances between nuclei are large is determined from the formulas

$$W_1 \approx -\frac{Z_1^2}{2n^2} - \frac{Z_2}{R} + \frac{3}{2}\,\frac{(n_1 - n_2)\,n}{Z_1}\,\frac{Z_2}{R^2},$$
$$W_2 \approx -\frac{Z_2^2}{2n'^2} - \frac{Z_1}{R} + \frac{3}{2}\,\frac{(n_1' - n_2')\,n'}{Z_2}\,\frac{Z_1}{R^2}, \tag{46}$$

where W_1 and W_2 correspond to the states in which the electron is located at the nucleus Z_1 or Z_2, respectively, as $R \to \infty$. The dependence

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*To prove this statement it is essential that the radial Coulomb functions satisfy the relation

$$\int_0^\infty v_{N,l}(r)\,v_{N,l+2}(r)\,\frac{dr}{r} = 0.$$

This relation can be derived from an analysis of the integrals of the generating function of the Laguerre polynomials.

on m appears in terms of order R^{-4}, corresponding to the second approximation for the Stark effect.

Knowing the arrangement of the terms at large and small distances [see (46) and (45)] and using formulas (39) — (42), which establish the connection between the terms, we can schematically represent the course of the terms at medium distances between nuclei. Figure 2 shows the course of the σ terms for the case $Z_1 = 2$ and $Z_2 = 3$, from which we can infer the presence of a large number of intersections. Particular interest attaches to intersections of terms corresponding, as $R \rightarrow \infty$, to states in which the electron is at different nuclei, for example 3pσ and 3dσ, 4fσ and 3sσ, etc. The presence of such intersections influences appreciably the probability of charge exchange in atomic collisions.

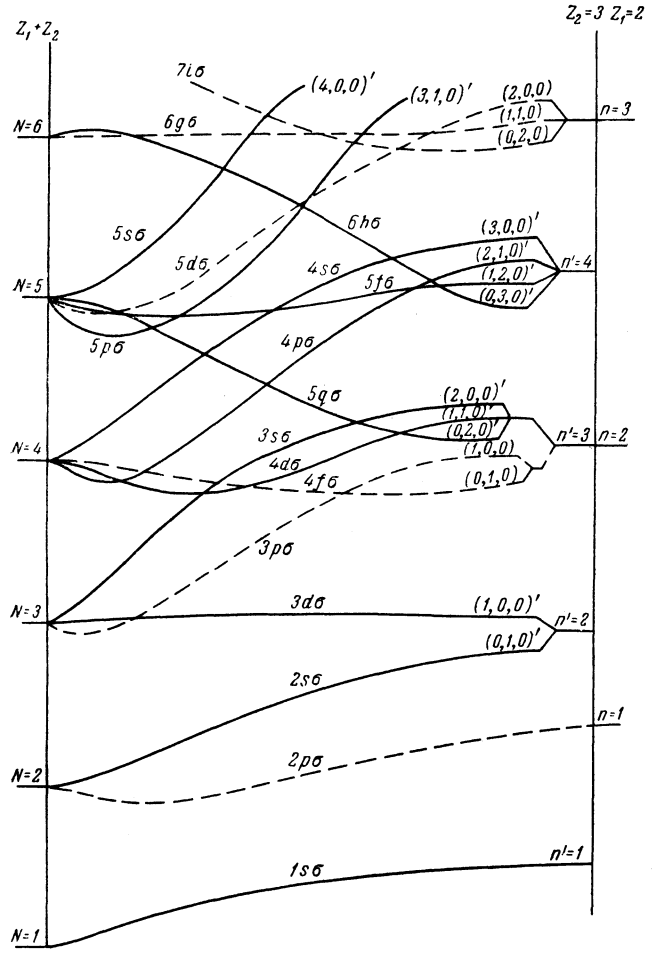

FIG. 2. σ terms for the case $Z_1 = 2, Z_2 = 3$. The parentheses contain the parabolic quantum numbers (n_1, n_2, m). The quantum numbers pertaining to the nucleus Z_2 are primed.

Let us consider especially the case $Z_1 = 1$, $Z_2 = Z > 1$, which is of practical interest in many of the problems mentioned in the introduction. Assume that the electron is on the hydrogen K orbit at infinity. The corresponding term (including the nuclear interaction $Z_1 Z_2/R$) behaves as $(-\frac{1}{2} - 9Z^2/2R^4)$ at large distances, and yields Coulomb repulsion of the nuclei at small distances. On the other hand, the terms corresponding at infinity to the states of the electron at the Z nucleus, increase at large distances as $-Z^2/2n^2 + (Z-1)/R$ with decreasing R. Therefore, at sufficiently large Z, some terms of the nucleus Z, lying at infinity below the K level of the hydrogen atom, should intersect the corresponding hydrogen term. [From formulas (39) — (42) it follows that when R = 0 the term corresponding to the K orbit of the hydrogen atom lies above those terms of the nucleus Z, which were located below this term at $R = \infty$, i.e., the terms should intersect twice (see Fig. 3).]

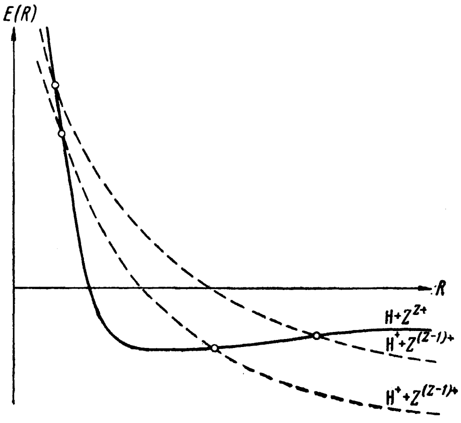

FIG. 3

This intersection occurs apparently even for $Z \geq 3$ [it is known to be missing in the case of the molecule HeH^{++}, see reference (8)] and should assure a greater charge-exchange probability in collisions between the hydrogen atom and the nucleus Z.

For terms corresponding to excited levels of the hydrogen atom, cases of intersection are encountered more frequently. The rapid transfer of negative mesons from hydrogen by the nuclei $Z > 1$ (see reference 9) is apparently due to precisely this circumstance.

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APPENDIX

WAVE FUNCTIONS FOR THE DEGENERATE CASE

In the case when the parabolic quantum numbers of the atoms Z_1 and Z_2 are equal, $n_1 = n_1'$ and $m = m'$, and the principal quantum numbers satisfy the relation $Z_1/n = Z_2/n'$ (i.e., the energy levels of the isolated atoms coincide), the wave function in the two-center problem can be approximately written in the form of a linear combination of the corresponding atomic functions ψ_1 and ψ_2:

$$\Psi = a\psi_1 + b\psi_2, \tag{A.1}$$

where

$$\psi_1 = C_1 (r_1 + z_1)^{|m|/2} e^{-Z_1 (r_1+z_1)/2n} F(-n_2;\ |m| + 1;\ Z_1 (r_1 + z_1)/n) \times (r_1 - z_1)^{|m|/2} e^{-Z_1 (r_1-z_1)/2n} F(-n_1;\ |m| + 1;\ Z_1 (r_1 - z_1)/n) e^{im\varphi}, \tag{A.2}$$

$$C_1 = \left(\frac{Z_1}{n}\right)^{|m|+3/2} \frac{1}{(m!)^2} \left[\frac{(n_1 + |m|)!\,(n_2 + |m|)!}{\pi n\,(n_1)!\,(n_2)!}\right]^{1/2}, \tag{A.3}$$

the z axis is directed from the first nucleus to the second; analogous formulas hold for ψ_2 ($n_1 = n'$; $Z_1/n = Z_2/n'$).

Noting that near the first nucleus (as $R \to \infty$) we have

$$r_1 - z_1 \approx R(\xi - 1), \qquad r_1 + z_1 \approx R(1 + \eta),$$

and near the second nucleus

$$r_2 + z_2 \approx R(\xi - 1), \qquad r_2 - z_2 \approx R(1 - \eta),$$

we can represent the function (A.1) in the form (3):

$$\Psi = e^{-Z_1 R\xi/n} (\xi - 1)^{|m|/2} F(-n_1;\ |m| + 1;\ Z_1 R(\xi - 1)/n)\, Y(\eta), \tag{A.4}$$

$$Y(\eta) = aC_1 e^{-Z_1 R\eta/n} (1 + \eta)^{|m|/2} F(-n_2;\ |m| + 1;\ Z_1 R(1 + \eta)/n) + bC_2 e^{Z_1 R\eta/n} (1 - \eta)^{|m|/2} F(-n_2';\ |m| + 1;\ Z_1 R(1 - \eta)/n). \tag{A.5}$$

Depending on the sign of the ratio a/b, the function $Y(\eta)$ can have either $n_2 + n_2'$ or $n_2 + n_2' + 1$ roots in the interval $-1 < \eta < 1$.

Substituting (A.1) in the Schrödinger equation (1), we obtain the secular equation for the energy

$$(Z_2 K_2 + \varepsilon) a + (Z_1 A_1 + \varepsilon S) b = 0, \tag{A.6}$$

$$(Z_2 A_2 + \varepsilon S) a + (Z_1 K_1 + \varepsilon) b = 0. \tag{A.7}$$

Here

$$E = -\frac{Z_1}{2n^2} + \frac{Z_1 Z_2}{R} + \varepsilon, \quad K_1 = \int |\psi_2|^2 \frac{1}{r_1} d\tau, \quad K_2 = \int |\psi_1|^2 \frac{1}{r_2} d\tau, \quad S = \int \psi_1^* \psi_2 d\tau, \quad A_1 = \int \psi_1^* \psi_2 \frac{1}{r_1} d\tau, \quad A_2 = \int \psi_2^* \psi_1 \frac{1}{r_2} d\tau. \tag{A.8}$$

Noting that the quantities A_1, A_2, and S are exponentially small compared with K_1 and K_2 (accurate to terms of order R^{-2}; $K_1 \approx K_2 \approx 1/R$), we can represent the solutions (A.6) in the form

$$\varepsilon_{\mathrm{I}} = -Z_2 K_2 + \frac{Z_2 (A_2 - SK_2)(Z_1 A_1 - Z_2 SK_2)}{Z_1 K_1 - Z_2 K_2}, \tag{A.9}$$

$$\left(\frac{b}{a}\right)_{\mathrm{I}} = -\frac{Z_2 (A_2 - SK_2)}{Z_1 K_1 - Z_2 K_2} \approx \frac{Z_2 R}{Z_2 - Z_1} (A_2 - SK_2); \tag{A.10}$$

$$\varepsilon_{\mathrm{II}} = -Z_1 K_1 - \frac{Z_1 (A_1 - SK_1)(Z_2 A_2 - Z_1 SK_1)}{Z_1 K_1 - Z_2 K_2}, \tag{A.11}$$

$$\left(\frac{a}{b}\right)_{\mathrm{II}} = \frac{Z_1 (A_1 - SK_1)}{Z_2 K_1 - Z_2 K_2} \approx -\frac{Z_1 R}{Z_2 - Z_1} (A_1 - SK_1). \tag{A.12}$$

It is seen from the foregoing expressions that the solution marked by the subscript I corresponds as $R \to \infty$ to the state for which the electron is at the nucleus Z_1 ($b/a \to 0$), while solution II corresponds to the state with the electron at the nucleus Z_2 ($a/b \to 0$). In this lies the essential difference between the case $Z_1 \neq Z_2$ and the case $Z_1 = Z_2$, for which the function (A.1) remains, as $R \to \infty$, a symmetrical or antisymmetrical combination of ψ_1 and ψ_2.

Confining ourselves in the calculation of the quantities in (A.8) to the members of highest order in R ($R \gg 1$), we obtain according to (A.10) and (A.12)

$$\left(\frac{b}{a}\right)_{\mathrm{I}} \approx (-1)^{n_2+n_2'} \frac{Z_2}{Z_2 - Z_1} \left(\frac{2Z_1}{n}\right)^{n_2+n_2'+1/2} \times \frac{2^{|m|+1/2}}{[nn'(n_2)!\,(n_2')!\,(n_2 + |m|)!\,(n_2' + |m|)!]^{1/2}} \times \frac{\Gamma(n_2 + |m|/2 + 3)\,\Gamma(n_2' + |m|/2 + 1)}{(n_2 + n_2' + |m| + 3)!} R^{n_2+n_2'+|m|+2} e^{-Z_1 R/n}, \tag{A.13}$$

$$\left(\frac{a}{b}\right)_{\mathrm{II}} \approx (-1)^{n_2+n_2'+1} \frac{Z_1}{Z_2 - Z_1} \left(\frac{2Z_1}{n}\right)^{n_2+n_2'+1/2} \times \frac{2^{|m|+1/2}}{[nn'(n_2)!\,(n_2')!\,(n_2 + |m|)!\,(n_2' + |m|)!]^{1/2}} \times \frac{\Gamma(n_2 + |m|/2 + 1)\,\Gamma(n_2' + |m|/2 + 3)}{(n_2 + n_2' + |m| + 3)!} R^{n_2+n_2'+|m|+2} e^{-Z_1 R/n} \tag{A.14}$$

The functions $F(-n_2;\ |m| + 1;\ Z_1 R(1 + \eta)/n)$ and $F(-n_2';\ |m| + 1;\ Z_1 R(1 - \eta)/n)$ in (A.5) have respectively n_2 and n_2' roots lying near the nuclei Z_1 and Z_2. If the addition of these functions does not give rise to an additional root in $Y(\eta)$, the sign of the ratio a/b should be $(-1)^{n_2+n_2'}$. Taking this remark into consideration, we can readily deduce from formulas (A.13) and (A.14) that the additional root arises when the electron is at the nucleus with the greater charge.

We note that this conclusion agrees with the oscillator theorem, since, as can be seen from (A.9) and (A.11), the term corresponding at large R to an electron at the nucleus with the greater charge lies $|Z_1 - Z_2|/R$ higher than the corresponding term for the electron at the nucleus with the smaller charge.

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