WAVE FUNCTIONS AND ELECTRON TERMS OF MOLECULAR ION H_2^+ FOR LARGE INTERNUCLEAR DISTANCES

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Submitted to JETP editor December 14, 1966

J. Theoret. Phys. (U.S.S.R.) 52, 1368–1377

The electronic terms and wave functions of the molecular ion H_2^+ in the ground and upper states are studied by the comparison method, the distance between the nuclei being assumed large. Exponential splitting of g and u terms is found with an accuracy to $O(R^{-2}e^{-R/n})$. The results are compared with numerical calculations and the limits of applicability of the theory are discussed. The results can be employed for studying collisions between protons and excited hydrogen atoms.

THE molecular ion H_2^+ is of great theoretical and practical interest. Knowledge of its terms is important for the study of the mechanisms of dissociation accompanied by formation of highly excited H atoms; the manner in which the symmetrical and antisymmetrical terms move apart asymptotically at large internuclear distances determines the resonant charge exchange in slow $H^+ + H$ collisions. The H_2^+ ion, when viewed as the simplest single-electron molecular system, is also the basic model for checking approximate quantum-chemistry methods.

Several recently published theoretical papers are devoted to the study of the properties of H_2^+ at large internuclear distances[1-5] and also to calculations.[6-8] In [1,2], attention was called to the fact that the LCAO[1)] method gives an asymptotically incorrect value of the splitting of the terms $1s\sigma_g$ and $2p\sigma_u$, in connection with the fact that the main contribution to this splitting is made by the subbarrier region between the centers. It is therefore important to determine more accurately the wave functions in this region, as was indeed done in [1,2], where the correct value of the splitting was obtained for the lower terms. Smirnov[3] generalized the formula for term splitting to include excited states. Ovchinnikov and Sukhanov[4] proposed a method for calculating the succeeding terms of the asymptotics of the wave functions and the terms of the states $1s\sigma_g$ and $2p\sigma_u$, and wrote out a formula for the spacing of these terms, accurate to $O(R^{-2}e^{-R})$. We note that none of the cited papers gives exact criteria for the applicability of the derived expressions.

In this paper we construct uniform asymptotic expressions for the wave functions, and obtain the magnitude and splitting of the ground and excited terms of the H_2^+ ion with an accuracy higher than in all the preceding calculations. We also write out the limits of applicability of the obtained expressions. We use here the standard-equation method with modifications proposed by one of the authors.[9,10] A mathematical derivation of the expansions will be published elsewhere.

1. FORMULATION OF PROBLEM

The stationary Schrödinger equation for the H_2^+ in the adiabatic approximation

$$\left(\frac{1}{2}\Delta+\frac{1}{r_a}+\frac{1}{r_b}+E\right)\Psi=0$$

is separable in prolate spheroidal coordinates

$$\xi=\frac{r_a+r_b}{R}(1\leqslant\xi<\infty),\quad \eta=\frac{r_a-r_b}{R}(-1\leqslant\eta\leqslant 1),$$
$$\varphi=\operatorname{arctg}\frac{y}{x}(0\leqslant\varphi<2\pi).$$

Here R is the internuclear distance and r_a and r_b is the distance from the electron to the centers a and b, respectively.

We seek a wave function in the form

$$\Psi=\frac{U(\xi)}{\sqrt{\xi^2-1}}\frac{V(\eta)}{\sqrt{1-\eta^2}}\frac{e^{\pm im\varphi}}{\sqrt{2\pi}},\qquad(1)$$

and obtain in this case the following equation for the functions $U(\xi)$ and $V(\eta)$:

$$U''+\left[-\frac{h^2}{4}+\frac{h(\rho\xi-\lambda)}{\xi^2-1}+\frac{1-m^2}{(\xi^2-1)^2}\right]U=0,\qquad(2)$$

[1)]Method of constructing molecular orbitals in the form of a linear combination of atomic orbits.

$$V'' + \left[-\frac{h^2}{4} + \frac{h\lambda}{1-\eta^2} + \frac{1-m^2}{(1-\eta^2)^2}\right]V = 0, \quad (3)$$

where $E = -2/\rho^2$ is the energy, $h = \sqrt{-2ER}$, λh is the separation constant, and $m = 0, 1, 2, \ldots$ is the modulus of the magnetic number.

In order for Ψ to be a bounded function, the solutions (2) and (3) must satisfy the conditions

$$U(\xi)|_{\xi=1} = 0, \quad U(\xi)_{\xi\to\infty} \to 0, \quad (4)$$

$$V(\eta)|_{\eta=\pm 1} = 0. \quad (5)$$

Since Eq. (3) and the boundary condition (5) are not altered by the substitution $\eta \to -\eta$, the function $V(\eta)$ will have a definite parity: Symmetrical solutions will satisfy the conditions

$$V_g'|_{\eta=0} = 0, \quad V_g|_{\eta=-1} = 0, \quad (6)$$

and antisymmetrical ones

$$V_u|_{\eta=0} = 0, \quad V_u|_{\eta=-1} = 0. \quad (6')$$

Thus, the determination of the function $\Psi(\xi, \eta, \varphi)$ reduces to boundary-value problems for the equations (2) and (3) with conditions (4) and (6), and now $\eta \in [-1, 0]$.

The procedure for obtaining the solution will differ somewhat from that used in physics for H_2^+. It is customary to obtain independently the separation constants from (2) and (3) and equate them to obtain the energy spectrum of the problem. At the same time, in analogy with the spherically-symmetrical case, it is more convenient to substitute into the quasi-radial equation (2) the separation constant obtained from the quasi-angular equation (3) (cf. $l(l+1)$), all the more since (3) does not contain the specific Coulomb feature of the problem, being an equation for oblate angular spheroidal functions.[11, 12]

It is more convenient mathematically to assume in the intermediate derivations that the independent parameter is h, putting $E = E(h)$, $R = R(h)$, and $\lambda = \lambda(h)$. We shall seek the asymptotic behavior of the problems (2), (4), and (3), (6) relative to the large parameter $h = \sqrt{-2ER}$, i.e., for large internuclear distances and not too high states. In the final formulas the energy will be expressed in the form of a series that depends on R.

2. METHOD OF FINDING THE ASYMPTOTIC FORMS

The asymptotic form of the boundary value problem for the equation

$$\psi''(h, x) + h^2 p^2(E, h, x)\psi(h, x) = 0 \quad (7)$$

as $h \to \infty$ is constructed in the following manner.[10] We first separate the spectral region of interest to us. We then construct a standard equation, which should have the same transition points as the initial equation on the considered interval of variation of the independent variable. By transition points we mean here the zeroes and poles of the function $p^2(E, h, x)$. In this case, if the distance between two points of the transition is of the order of $O(h^{-2})$ and less, they are regarded as one transition point. To obtain an asymptotic form which is uniform with respect to the variable x, it is also necessary that the standard equation have at infinity a singularity of the same type as the initial equation.

The solution of the initial problem is sought in the form of an asymptotic series, for which the form is specified by the standard solution. There are two possibilities here. In the first method, the solution is represented by an asymptotic series multiplied by the standard solution, and the coefficients of the expansion are determined in succession by substituting into the equation. The second method was proposed by Cherry[13] and consists of expressing the solution of the initial problem directly in terms of the standard solution, in which, however, the argument is an asymptotic series. The second method is preferable in our case, since the "quantum conditions" (agreement of the transition points of the initial and standard equations) are not integral (of the type of the Bohr-Sommerfeld classical conditions). We note that the obtained asymptotic form is not uniform only in the vicinity of the zeroes of the solution.

3. ASYMPTOTIC EXPANSION FOR THE QUASI-ANGULAR FUNCTIONS. EXPONENTIAL SPLITTING OF g AND u FUNCTIONS

Equation (3) can be regarded as a one-dimensional Schrödinger equation with potential

$$v(\eta) = -\frac{h\lambda}{1-\eta^2} - \frac{1-m^2}{(1-\eta^2)^2}.$$

We confine ourselves to the case

$$h/4 \gg \lambda, \quad (8)$$

i.e., to not very high eigenvalues, lying deep in the subbarrier region of the potential $v(\eta)$. We must then choose as the standard equation the Whittaker equation[14]

$$W'' + \left[-\frac{h^2}{4} + \frac{hk}{z} + \frac{1-m^2}{4z^2}\right]W = 0 \quad (9)$$

and seek the solution of (3) and (6) in the form

$$V(\eta) = [z'(\eta)]^{-1/2} M_{k,\, m/2}(hz(\eta)), \quad (10)$$

where the function $M_{k,\,m/2}(hz)$ is a solution of (9) which is regular at zero. (We shall subsequently change over to the independent variable $x = 1 + \eta$.)

We note that if $k = k_0 = n_2 + (m + 1)/2$, where $n_2 = 0, 1, 2, \ldots$, then the Whittaker functions are expressed in terms of Laguerre polynomials, so that the function $V(x)$ (10) goes over into the usual quasi-angular function of the hydrogen atom in parabolic coordinates with number n_2. Substituting the solution (10) in (1) and using the standard equation (9), we obtain for $z(x)$ the formal equation

$$\left(\frac{z'^2}{4}-\frac{1}{4}\right)+\frac{1}{h}\left(\frac{\lambda}{2x(1-x/2)}-\frac{kz'^2}{z}\right)+\frac{\tau}{h^2}\left[\frac{1}{x^2(1-x/2)^2}-\frac{z'^2}{z^2}\right]-\frac{1}{2h^2}\{z,x\}=0, \tag{11}$$

where $\{z, x\} = -{}^3/_2(z''/z')^2 + z'''/z'$ is the Schwartz derivative and $\tau = (1 - m^2)/4$. We require that the transition points coincide, i.e.,

$$z(x)\,|_{x=0}=0, \tag{12}$$

which yield a "quantum condition"

$$\lambda = 2kz'(0)+\frac{2\tau}{h}\left[\frac{z''(0)}{z'(0)}-1\right], \tag{13}$$

containing no integrals. We shall seek the solution of (11) with eigenvalues in the form of asymptotic expansions

$$z(x)=\sum_{l=0}^{\infty}\frac{z_l(x)}{h^l},\quad \lambda(k)=\sum_{l=0}^{\infty}\frac{\lambda_l(k)}{h^l}. \tag{14}$$

and then obtain from (11) a system of recurrent differential equations for the function $z_l(x)$:

$$\begin{gathered} z_0'=1,\\ z_1'=-\frac{\lambda_0}{x(1-x/2)}+\frac{2k}{x},\\ z_2'=-\frac{z_1'^2}{2}-\frac{\lambda_1}{x(1-x/2)}+\frac{2k}{x}\left(2z_1'-\frac{z_1}{x}\right)+\tau\frac{(1-x/4)}{x(1-x/2)},\\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots \end{gathered} \tag{15}$$

and from (13) a system for the eigenvalues $\lambda_l(k)$:

$$\begin{aligned} &\lambda_0 = 2kz_0'(0),\\ &\lambda_1 = 2kz_1'(0)-2\tau,\\ &\lambda_2 = 2kz_2'(0)+2\tau z_1''(0),\\ &\ldots\ldots\ldots\ldots \end{aligned} \tag{16}$$

Successive satisfaction of the conditions (16) ensures the existence of solutions for the corresponding equations in (15). It is easy to see that to determine $\lambda_l(k)$ it is not necessary to integrate (15) exactly, and it is sufficient to determine the first two terms of the Taylor series near $x = 0$. With an aim at taking into account the polarization term in the energy, we determine λ accurate to fourth order inclusive:

$$\lambda = 2k-\frac{2(k^2+\tau)}{h}-\frac{2k(k^2+\tau)}{h^2}-\frac{1}{h^3}(5k^4+6k^2\tau+k^2+\tau^2)-\frac{1}{h^4}\left[\frac{33}{2}k^5+23k^3\tau+\frac{17}{2}k^3+\frac{13}{2}k\tau^2+3k\tau\right]+O\left(\frac{1}{h^5}\right). \tag{17}$$

The corresponding expansion for $z(x)$ is

$$\begin{aligned} z(x)={}&x+\frac{2k}{h}\ln\left(1-\frac{x}{2}\right)+\frac{1}{h^2}\left[\frac{4k^2}{x}\ln\left(1-\frac{x}{2}\right)-\frac{k^2+\tau}{1-x/2}+3k^2+\tau\right]\\ &+\frac{1}{h^3}\left[\frac{4k^3}{-x^2}\ln^2\left(1-\frac{x}{2}\right)+\frac{4k}{x^2}(3k^2+\tau)\times\ln\left(1-\frac{x}{2}\right)+\frac{2k}{x}(3k+\tau)-\frac{2k(k^2+\tau)}{1-x/2}\right.\\ &\left.-\frac{k(k^2+\tau+1)}{2(1-x/2)^2}+\frac{k}{2}(10k^2+6\tau+1)\right]+\frac{z_4(x)}{h^4}+O\left(\frac{1}{h^5}\right). \end{aligned} \tag{18}$$

In view of the unwieldiness of the expression for $z_4(x)$, we present it only for the ground state ($k = {}^1/_2$):

$$\begin{aligned} z_4|_{k=1/2}={}&\frac{\ln^3(1-x/2)}{3x^3}-\frac{5}{2x^3}\ln^2\left(1-\frac{x}{2}\right)+\ln\left(1-\frac{x}{2}\right)\times\left[\frac{6}{x^3}-\frac{1}{2x^2}+\frac{1}{4x}+\frac{1}{8(1-x/2)}\right]-\frac{13}{24(1-x/2)^3}\\ &-\frac{9}{16(1-x/2)^2}-\frac{17}{16(1-x/2)}+\frac{3}{x^2}+\frac{9}{8x}+2\frac{5}{6}. \end{aligned} \tag{19}$$

We have thus determined the function $V(\eta)$ defined by (10), which satisfies Eq. (3) accurate to terms $O(h^{-4})$ and the boundary condition at $x = 1$. We stipulate that at $x = 0$ it is necessary to satisfy a condition which, with (10) taken into account, assumes the form

$$M'_{k,\,m/2}(hz)-\frac{1}{2h}\frac{z''}{z'^2}M_{k,\,m/2}(hz)\,|_{x=1}=0, \tag{20}$$

$$M_{k,\,m/2}(hz)\,|_{x=1}=0, \tag{20'}$$

thereby separating the symmetrical and antisymmetrical functions. The conditions (20) and (20′) are transcendental equations for k_g and k_u.

Let us consider in greater detail the antisymmetrical case. Since $z(x) \neq 0$ when $x = 1$, and h is a large parameter, we use the asymptotic form of the Whittaker function[14] and represent (20′) in the form

$$\left\{\frac{(-)^{k-(m+1)/2}(hz)^k e^{-hz/2}}{\Gamma(k+(m+1)/2)}\Sigma_- +\frac{e^{hz/2}(hz)^{-k}}{\Gamma(-k+(m+1)/2)}\Sigma_+\right\}_{x=1}=0, \tag{21}$$

where

$$\Sigma_{\mp} = \sum_{n=0}^{\infty}\left(\frac{1+m}{2}\mp k\right)_n\left(\frac{1-m}{2}\mp k\right)_n\frac{(\mp hz)^{\mp n}}{n!}.$$

We note that the second series, which has only positive terms, does not vanish in the interval under consideration. Dividing by this term and using the well known property of the gamma-function[14]

$$\Gamma\left(\frac{1}{2}-x\right)\Gamma\left(\frac{1}{2}+x\right)=\frac{\pi}{\cos\pi x},$$

we obtain

$$\frac{\cos\pi(k-m/2)}{\pi}=\frac{(-)^{k-(m+1)/2}e^{-hz}(hz)^{2k}\Sigma_-}{\Gamma((1+m)/2+k)\Gamma((1-m)/2-k)\Sigma_+}\Big|_{x=1}. \quad (22)$$

If we replace the right side by zero when $h\to\infty$, then k goes over into $k_0 = n_2 + (m + 1)/2$, where $n_2 = 0, 1, 2, \ldots$, so that we shall seek k_u in the form $k_u = k_0 + \delta k_u$. Iterating (22) with due allowance for the expansion (18), we get

$$\delta k_u=\frac{(2h)^{2k}e^{-h}}{n_2!(n_2+m)!}\left[1-\frac{3k^2+\tau}{h}+\frac{9k^4-10k^3+6k^2\tau-6k\tau+\tau^2-k}{2h^2}+O\left(\frac{1}{h^3}\right)\right]_{k=k_0} \quad (23)$$

For the ground state ($k_0 = 1/2$) we get

$$\delta k_u|_{k_0=1/2}=2he^{-h}\left[1-\frac{1}{h}-\frac{3}{4h^2}-\frac{7}{4h^3}+O\left(\frac{1}{h^4}\right)\right]. \quad (24)$$

Succeeding iterations of (22) lead to exponentials that are integral multiples and must be omitted in the asymptotic expansion. However, these exponentials are formally determined uniquely (they were written out for the terms $1s\sigma_g - 2p\sigma_u$ in [4]) and can become important in the study of the analytic properties of the problem in the complex h plane.

An analogous consideration of the g-terms leads to the expression $k_g = k_0 + \delta k_g$, with δk_g differing from δk_u only in sign, i.e.,

$$\delta k_g=-\delta k_u[1+O(1/h^4)]. \quad (25)$$

We were unable to prove such a symmetry in general form.

We call attention to the fact that the series Σ_- in the numerator of (22) could formally vanish. However, when the inequality $h/4 \gg \lambda$ is satisfied, this does not take place, since the function $M_{k0,\,m/2}(hz)$ cannot have any zeroes in the subbarrier region.

All the functions of k, such as z, λ, E, and others, acquire an exponential splitting corresponding to the g and u states, which can be determined by simple differentiation of these functions with respect to k, for example,

$$\delta E_{g,u}=\frac{\partial E}{\partial k}\Big|_{k=k_0}\delta k_{g,u}. \quad (26)$$

We emphasize also that since λ splits into λ_g and λ_u, the quasi-radial functions will be different for the g and u states even when $R\to\infty$.

4. ASYMPTOTIC FORM OF THE QUASI-RADIAL FUNCTIONS

Analyzing expression (2) we arrive at the same standard equation (9) as for the quasi-angular functions. The solutions of (2) and (4) will be sought in the form

$$U(\xi)=[y'(\xi)]^{-1/2}M_{\varkappa,\,m/2}(hy(\xi)) \quad (27)$$

If we choose $\kappa = n_1 + (m + 1)/2$, where $n_1 = 0, 1, 2, \ldots$, then the solution will decrease at infinity, and we shall be able to express the Whittaker function in terms of Laguerre polynomials. For the argument $u(\xi)$ we obtain the formal expression

$$\left(\frac{y'^2}{4}-\frac{1}{4}\right)+\frac{1}{h}\left(\frac{\xi\rho-\lambda}{\xi^2-1}-\frac{\varkappa y'^2}{y}\right)+\frac{\tau}{h^2}\left(\frac{4}{(\xi^2-1)^2}-\frac{y'^2}{y^2}\right)-\frac{1}{2h^2}\{y,\xi\}=0. \quad (28)$$

We require that all the transition points coincide, i.e., $y(\xi)|_{\xi=1} = 0$; this leads to the quantum conditions for ρ:

$$\rho=\left\{\lambda+2\varkappa y'+\frac{2\tau}{h}\left(\frac{y''}{y'}+1\right)\right\}_{\xi=1}. \quad (29)$$

As before, we seek y and ρ in the form of asymptotic expansions in reciprocal powers of h, and then we arrive at recurrence systems analogous to (15) and (16) for the successive expansion coefficients. We write out the final results for the function $y(\xi)$

$$y=(\xi-1)-\frac{2}{h}(2k+\varkappa)\ln\frac{\xi+1}{2}+\frac{1}{h^2}\left[\ln\left(\frac{\xi+1}{2}\right)\left[4(k+\varkappa)^2-\frac{4\varkappa(2k+\varkappa)}{\xi-1}\right]+\frac{2(2k+\varkappa)^2+2\tau}{\xi+1}-4k^2+\varkappa^2-\tau\right]+\frac{y_3(\xi)}{h^3}+\frac{y_4(\xi)}{h^4}+O\left(\frac{1}{h^5}\right). \quad (30)$$

and the eigenvalue ρ

$$\rho=2(k+\varkappa)-\frac{2}{h}(k+\varkappa)^2+\frac{2}{h^2}(k+\varkappa)^2(2\varkappa-k)-\frac{(k+\varkappa)^2}{h^3}[-(k+\varkappa)^2+6(k-\varkappa^2)+1]+\frac{(k+\varkappa)^2}{2h^4}[-33k^3+102k^2\varkappa-87k\varkappa^2-4\varkappa^3-17k+8\varkappa-18k\tau]+O\left(\frac{1}{h^5}\right). \quad (31)$$

The terms for ρ of order $O(h^{-3})$ and $O(h^{-4})$ were obtained without accurate integration, but with the aid of the expansion of the functions $y_3(\xi)$ and $y_4(\xi)$ in a Taylor series about $\xi = 1$.

5. ASYMPTOTIC EXPANSION FOR THE ENERGY. WAVE FUNCTIONS

We have thus obtained the function $\rho(h)$. If we return to the physical parameters $E = 2/\rho^2$ and $R = \rho h/2$, then we can obtain asymptotic expansions for $h = h(R)$ and $E = E(R)$. These are

$$h = \frac{R}{n}\left\{1 + \frac{n^2}{R} - \frac{n^3(n+3\Delta)}{2R^2} + \frac{n^4(3n\Delta+6\Delta^2+1)}{R^3} + O\left(\frac{1}{R^4}\right)\right\}, \quad (32)$$

$$E = -\frac{1}{2n^2} - \frac{1}{R} + \frac{3n\Delta}{2R^2} - \frac{n^2}{2R^3}[6\Delta^2 - n^2 + 1] - \frac{n^3}{16R^4}\{(17n^3 + 19n - 9m^2 n) + 39n^2\Delta - 3n\Delta^2 - 109\Delta^3 - 59\Delta + 9\Delta m^2\} + O\left(\frac{1}{R^5}\right). \quad (33)$$

We have gone over here to the quantum numbers which are customarily used to describe the Stark effect in hydrogen: $n = k + \kappa$ is the principal quantum number, $\Delta = n_1 - n_2 = \kappa - k$ is the electric number, where, as already mentioned, n_1 and n_2 are the parabolic quantum numbers.

The separation of the g and u terms is obtained by means of formula (26)

$$E_u - E_g = \frac{2}{n^3}\frac{e^{-R/n-n}}{n_2!(n_2+m)!}\left(\frac{2R}{n}\right)^{2n_2+m+1}\left\{1 + \frac{n}{4R}\times(3n^2+8\Delta n-3\Delta^2-1+m^2) + \frac{n^2}{32R^2}\times[(3n^2+8n\Delta-3\Delta^2)^2 - 4(7n^3+13n^2\Delta+21n\Delta^2-5\Delta^3) + 2(-27n^2+16n\Delta+3\Delta^2) - 4(7n-5\Delta)+1 + 2m^2(3n^2+8n\Delta-3\Delta^2-6\Delta+2n-1)+m^4]\right\}. \quad (34)$$

Of certain importance in the theory of resonant symmetrical charge exchange $H^+ + H$ is the separation of the $1s\sigma_g - 2p\sigma_u$ terms, which is given by

$$E_u - E_g = \frac{4}{e}Re^{-R}\left\{1 + \frac{1}{2R} - \frac{25}{8R^2} - \frac{131}{48R^3} + O\left(\frac{1}{R^4}\right)\right\}. \quad (35)$$

The wave functions, as solutions of the boundary value problem, will be automatically orthogonal. We write them out after normalization in the first approximation in R^{-1}:

$$\Psi(\xi,\eta,\varphi) = \sqrt{2}\,m!\left[\frac{n_2!}{(n_2+m)!}\right]^{3/2}\left[\frac{n_1!}{(n_1+m)!}\right]^{1/2} \times \frac{e^{-hy/2}(hy)^{(m+1)/2}L_{n_1}{}^m(hy)}{\sqrt{y'(\xi^2-1)}}\frac{M_{k,m/2}(hz)}{\sqrt{z'(1-\eta^2)}}\frac{e^{im\varphi}}{\sqrt{2\pi}} \times\left\{1 - \frac{2kn}{R} + O\left(\frac{1}{R^2}\right)\right\}, \quad (36)$$

where z, z′, y, and y′ are given by (18) and (30) with allowance for the reexpansion (32) of h in terms of R. The criterion for the applicability of the resultant formulas is the inequality

$$R \gg 8k_0 n, \quad (37)$$

which follows from (8). Physically it means that we have confined ourselves to states whose energy is much lower than the potential in the central region between the Coulomb centers.

6. DISCUSSION OF RESULTS

The power law expansion (33) describes the Stark effect for the hydrogen atom in an inhomogeneous field of a point charge $Z = +1$. The term proportional to R^{-2} gives the contribution of the linear dipole interaction and coincides with the linear Stark effect. The quadrupole moment of the atom leads to an interaction proportional to R^{-3}, which vanishes for the ground state, and also for certain excited states (for example, $n = 5$, $|n_1 - n_2| = 2$). The polarization term, which is proportional to R^{-4}, describes the linear octupole interaction and the quadratic dipole interaction. The octupole interaction for states that are symmetrical with respect to the plane $z = 0$, i.e., when $n_1 = n_2$, vanishes, and the remaining quadratic dipole interaction coincides with the quadratic Stark effect in a homogeneous field.[1]

The exponentially small separation of the g and u terms (34) agrees in first order with the expression obtained by Smirnov[3, 15] with the aid of the hypervirial relation proposed by Landau and Lifshitz[1] for the difference $E_g - E_u$.[1] The second

Table I. Difference $E_u - E_g$ for the ground state (terms $1s\sigma_g - 2p\sigma_u$) as a function of the internuclear distance.

R	$E_u - E_g$		
	Peek [7]	Ovchinnikov and Sukhanov [4]	Present work
5	4,7129 (−2)	4,8336 (−2)	4,7254 (−2)
10	6,7766 (−4)	6,8060 (−4)	6,7878 (−4)
15	6,8761 (−6)	6,8834 (−6)	6,8779 (−6)
20	6,1678 (−8)	6,1703 (−8)	6,1682 (−8)
25	5,1847 (−10)	5,1857 (−10)	5,1848 (−10)
30	4,1850 (−12)	4,1856 (−12)	4,1852 (−12)
35	3,2852 (−14)	3,2855 (−14)	3,2853 (−14)
40	2,5269 (−16)	2,5270 (−16)	2,5269 (−16)

Table II. Energy of the states $2s\sigma_g$ and $3p\sigma_u$ ($k_0 = 1/2$, $\kappa = 3/2$, $m = 0$) for $R = 10$ atomic units

	Bates et al. [16]	Present work
$-\left(\frac{E_g + E_u}{2}\right)$	2,026 (−1)	2,088 (−1)
$E_u - E_g$	4,12 (−3)	4,50 (−3)

terms of the expansions of [3, 15] differ, but a comparison of the splitting of the eigenvalues of λ with the Meixner and Schafke formula[11] proves the correctness of our expression. Calculations for the ground state (35) reveal agreement with the results of all the preceding authors in that region where they overlap.

Table I shows a comparison of the results for the splitting of the ground state, obtained numerically with an electronic computer by Peek,[7] obtained from the formulas of Ovchinnikov and Sukhanov,[4] and obtained from our formulas (35). Criterion (37) yields $R \gg 4$ for the ground state, and therefore we give values $R \geq 5$. We see that allowance for the last term in the expansion (36) improves the accuracy by approximately one order of magnitude.

The excited states of H_2^+ were calculated only in [16], where the internuclear distances did not exceed ten atomic units. By virtue of the criterion (37), we can carry out the comparison only for the terms $2s\sigma_g$ and $3p\sigma_u$ ($k_0 = 1/2$, $\kappa = 3/2$, $m = 0$), for which $R \gg R_{cr} = 8$ atomic units. Table II lists the values of $-(E_g + E_u)/2$ and $E_u - E_g$ for these terms at $R = 10$ at. units. The comparison indicates good accuracy of the presented expansions.

We propose to consider in the future, by a similar method, the behavior of terms near the peak of the barrier, and also the continuous spectrum of the problem.

The authors are grateful to V. S. Buldyrev and Yu. N. Demkov for interest in the work and useful discussions.

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Translated by J. G. Adashko
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