Reports of the Academy of Sciences of the USSR

A. A. OVCHINNIKOV, A. D. SUKHANOV

1964

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1964. Volume 157, No. 5

PHYSICS

A. A. OVCHINNIKOV, A. D. SUKHANOV

ON THE QUESTION OF WAVE FUNCTIONS AND ELECTRONIC TERMS OF THE MOLECULAR HYDROGEN ION

(Presented by Academician N. N. Bogolyubov, 13 IV 1964)

1. It is known that progress in the theory of atoms is due to a considerable extent to the fact that the problem of an electron in the field of a single Coulomb center has been solved exactly. One may hope that an exact solution of the simplest one-electron molecular problem will likewise lead to progress in the theory of molecules. Such a problem is that of the ion H_2^+, i.e., the problem of an electron in the field of two fixed Coulomb centers. Meanwhile, no exact solution of this problem exists, and the LCAO method gives only approximate expressions for the wave functions and electronic terms (see, for example, ([1])). Recently it was shown ([2], [3]) that these expressions are not satisfactory even for large distances R between the nuclei. However, in ([2], [3]), the correct wave functions for large R were not obtained and there is no regular procedure for calculating the electronic terms. In this connection it is of interest to obtain such a method for calculating the wave functions and electronic terms for the ion H_2^+.

The Schrödinger equation for the ion H_2^+, after separation of variables in elliptic coordinates, takes the form

$$\frac{d}{d\xi}\left[(\xi^2-1)\frac{dX(\xi)}{d\xi}\right]+\left[-\frac{m^2}{\xi^2-1}+2R\xi+p^2(1-\xi^2)+A\right]X(\xi)=0; \quad (1)$$

$$\frac{d}{d\eta}\left[(1-\eta^2)\frac{dY(\eta)}{d\eta}\right]+\left[-\frac{m^2}{1-\eta^2}+p^2(\eta^2-1)-A\right]Y(\eta)=0, \quad (2)$$

where the wave function is $\Psi(\xi,\eta,\varphi)=X(\xi)Y(\eta)e^{im\varphi}$, and the energy is $W=-2p^2/R^2$. Here the variables vary within the limits $1\le\xi<\infty$, $-1\le\eta\le1$, $0\le\varphi\le2\pi$, and the quantity A is the separation constant. In what follows, since we shall consider only the two lowest levels (as $R \to \infty$), we restrict ourselves to the case $m = 0$.

Until now these equations have been solved only by numerical methods ([4–6]). We shall find solutions of equations (1) and (2) in the form of expansions for large R. In doing so, the solution is connected with taking into account two physically different effects. First, with taking into account the Stark effect for the hydrogen atom in the field of the other nucleus. This will lead to the appearance in the wave functions and terms of expansion terms in powers of $1/R$, which corresponds to the usual expansion in multipoles and does not lead to a chemical bond. Second, with taking into account the effect of subbarrier penetration of the electron from one nucleus to the other, which naturally must lead to exponentially small terms of the type e^{-R}. Thus it is reasonable to seek the solution for the wave functions and terms in the form of double series

$$\Psi(\xi,\eta) = \sum_{i,j=0}^{\infty} a_{ij}(\xi,\eta)\mu^i\nu^j; \qquad W = \sum_{i,j=0}^{\infty} b_{ij}\mu^i\nu^j, \tag{3}$$

where $\mu \sim 1/R$, and $\nu \sim e^{-R}$. Below we shall be concerned with determining the functions $a_{ij}(\xi,\eta)$ and the coefficients b_{ij}.

2. Let us first consider equation (1). As will be seen from what follows, a more convenient expansion parameter is not R, but p, with $p \sim R$ as $R \to \infty$. If one makes the natural substitution $X(\xi) = e^{-p\xi}\Phi(\xi)$, then the equation obtained from (1) is conveniently solved by dividing the range of variation of ξ into two parts: region I near the singular point $\xi = 1$ and region II, where $\xi \gg 1$.

In region II we write equation (1) as

$$(1-\xi^2)\Phi'(\xi) + \left[\left(\frac{R}{p}-1\right)\xi + \frac{A}{2p}\right]\Phi(\xi) = -\frac{1}{2p}\left[(\xi^2-1)\Phi''(\xi) + 2\xi\Phi'(\xi)\right] \tag{4}$$

and shall carry out iterations, regarding the right-hand side as small. Then the first approximation gives

$$\Phi(\xi) = (\xi+1)^\sigma\left(\frac{\xi-1}{\xi+1}\right)^\alpha; \qquad \sigma = \frac{R}{p}-1; \qquad \alpha = \frac{A+2\sigma p}{4p}. \tag{5}$$

On the other hand, in region I, making the substitution $x = 2p(\xi-1)$, we obtain the equation [7]

$$x\Phi''(x) + (1-x)\Phi'(x) + \alpha\Phi(x) =$$

$$= \frac{1}{4p}\left[-x^2\Phi''(x) + (x^2-2x)\Phi'(x) - \sigma x\Phi(x)\right]. \tag{6}$$

Regarding the right-hand side as small, in the first approximation we obtain an equation whose solution, taking into account the conditions of boundedness at $x=0$ and $x\to\infty$, is $\Phi(x) = L_n(x)$, where $L_n(x)$ are Laguerre polynomials. For the two states considered [7], $n=\alpha=0$.

Applying iterations in region II as many times as necessary, we obtain that

$$\Phi(\xi) = (\xi+1)^\sigma\left\{1 + \frac{\sigma^2}{4p}\frac{\xi-1}{\xi+1} + \frac{\sigma^2}{(4p)^2}\left[2(\sigma-1)\frac{\xi-1}{\xi+1} + \frac{1}{2}(\sigma-1)^2\left(\frac{\xi-1}{\xi+1}\right)^2\right] + \right.$$

$$\left. + \frac{\sigma^2}{(4p)^3}\left[(5\sigma^2-12\sigma+6)\frac{\xi-1}{\xi+1} + (\sigma-1)^2(2\sigma-3)\left(\frac{\xi-1}{\xi+1}\right)^2 + \frac{1}{6}(\sigma-1)^2(\sigma-2)^2\left(\frac{\xi-1}{\xi+1}\right)^3\right] + \ldots\right\}. \tag{7}$$

It is not difficult to see that, although this solution was obtained in region II, it is also valid in region I. At the same time, for A we obtain

$$A = -2\sigma p - \sigma - \frac{\sigma^2}{4p} - \frac{2\sigma^2(\sigma-1)}{(4p)^2} - \frac{\sigma^2(5\sigma^2-12\sigma+6)}{(4p)^3} + \ldots \tag{8}$$

3. Let us now turn to the solution of equation (2). Although in appearance it resembles equation (1), unlike the latter the singular points $\eta=\pm1$, and not the points $(+1)$ and ∞, fall within the domain of definition of the function $Y(\eta)$. In addition, equation (2) is invariant with respect to a change in the sign of η. This means that there exist two linearly independent solutions $Y_1(\eta)$ and $Y_2(\eta) = Y_1(-\eta)$, and therefore the general solution for the two lowest states should be sought in the form $Y(\eta) = Y_1(\eta) \pm Y_2(\eta)$. Restricting ourselves to the consideration of $Y_1(\eta)$, we make the substitution $Y_1(\eta) = e^{p\eta}\widetilde{\Phi}(\eta)$. Further, as above, we divide the range of variation of η into two parts: region I near $\eta=+1$ and region II, where $1>\eta>-1$.

In region II, equation (2) is conveniently rewritten as

$$(1-\eta^2)\widetilde{\Phi}'(\eta) - 2\beta\widetilde{\Phi}(\eta) + (1-\eta)\widetilde{\Phi}(\eta) =$$

$$= \frac{1}{2p}\left[(\eta^2-1)\widetilde{\Phi}''(\eta) + 2\eta\widetilde{\Phi}'(\eta)\right]. \tag{9}$$

The first approximation to (9) has the form

$$\widetilde{\Phi}(\eta) = \frac{2}{1+\eta}\left(\frac{1-\eta}{1+\eta}\right)^{-\beta}; \qquad \beta = \frac{A+2p}{4p},$$

and, taking $Y_2(\eta)$ into account, for $Y(\eta)$ we obtain

$$Y(\eta) = \frac{2e^{p\eta}}{1+\eta}\left(\frac{1-\eta}{1+\eta}\right)^{-\beta} \pm \frac{2e^{-p\eta}}{1-\eta}\left(\frac{1+\eta}{1-\eta}\right)^{-\beta}. \tag{10}$$

In region I, after the substitution $y = 2p(1-\eta)$, equation (2) takes the form [7]

$$y\widetilde{\Phi}''(y) + (1-y)\widetilde{\Phi}'(y) - \beta\widetilde{\Phi}(y) =$$

$$= \frac{1}{4p}\left[y^2\widetilde{\Phi}''(y) + (2y-y^2)\widetilde{\Phi}'(y) - y\widetilde{\Phi}(y)\right]. \tag{11}$$

In the first approximation in $1/4p$, the solution of (11) that is bounded at $y = 0$ is a degenerate hypergeometric function, i.e. $\tilde{\Phi}(y) = CF(\beta; 1; y)$. If one chooses a solution that is also bounded at infinity, then, as in the preceding case, for the two levels considered, (7) $\beta = -n = 0$, and $\widetilde{\Phi}(y) = L_0(y)$.

As a result, the solution of equation (9), to within power terms in $1/4p$, can be found in the same way as above, and it has the form

$$\tilde{\Phi}_0(\eta) = \frac{2}{1+\eta}\left\{1 + \frac{1}{4p}\frac{1-\eta}{1+\eta} + \frac{1}{(4p)^2}\left[4\frac{1-\eta}{1+\eta} + 2\left(\frac{1-\eta}{1+\eta}\right)^2\right]\right.$$
$$\left. + \frac{1}{(4p)^3}\left[23\frac{1-\eta}{1+\eta} + 20\left(\frac{1-\eta}{1+\eta}\right)^2 + 6\left(\frac{1-\eta}{1+\eta}\right)^3\right] + \dots\right\}. \tag{12}$$

Analogously, the corresponding part A is equal to

$$A_0 = -2p + 1 + \frac{1}{4p} + \frac{4}{(4p)^2} + \frac{23}{(4p)^3} + \dots \tag{13}$$

However, it should be noted that in the present case y in (11) cannot tend to infinity, since $0 \leq y \leq 4p$. Therefore, as will now become clear, the parameter β, in addition to terms of the form $(1/4p)^n$, must also contain exponentially small terms. In particular, in zeroth order in $1/4p$, instead of $\beta = 0$ one should put $\beta = \lambda$, where λ is exponentially small. As is known, the function $F(\beta; 1; y)$ grows exponentially as y increases, so that $Y(y)$ behaves as

$$\frac{e^{y/2}}{y}\frac{\lambda y^{\lambda}}{\Gamma(1+\lambda)},$$

where $\Gamma(1+\lambda)$ is the gamma function. Therefore, in order that for $y \sim 4p$ the function $Y(y)$ be bounded, the parameter λ must be $\sim 4pe^{-2p}$.

In view of the exponential smallness of λ, we shall seek $\tilde{\Phi}(y)$ in the form

$$\tilde{\Phi}(y) = 1 + \lambda \int_0^y \frac{e^t - 1}{t}\, dt + \tilde{C}. \tag{14}$$

The parameters λ and $\tilde{C}$ entering here can be determined from matching with the corresponding solution in region II. For this purpose let us rewrite $Y(\eta)$ of the form (10) in the variables y. Then, retaining terms of order λ, we have

$$Y(y) = e^{p-y/2} \left\{ 1 - \lambda \ln \frac{y}{4p} \mp \frac{4pe^{-2p}}{y} e^y \right\}. \tag{15}$$

At the same time, in region I, in the limit $y \to \infty$ (taking (14) into account),

$$Y(y) = e^{p-y/2} \left\{ 1 + \lambda \frac{e^y}{y} - \lambda \ln y - \lambda\gamma + \tilde{C} \right\}, \tag{16}$$

where γ is Euler' s constant. Comparing (15) and (16), we obtain that

$$\lambda = \mp 4pe^{-2p}; \qquad \tilde{C} = \lambda(\gamma + \ln 4p).$$

Carrying out the same procedure in the following orders in the parameters λ and $1/4p$, we obtain in region II the expression

$$Y_1(\eta) = e^{p\eta} \left(\frac{1+\eta}{1-\eta} \right)^{\lambda} \left\{ \tilde{\Phi}_0(\eta) + \frac{4\lambda}{4p} \frac{1}{1+\eta} \left[\ln \frac{1-\eta}{1+\eta} - \frac{1-\eta}{1+\eta} + \frac{1}{2} \right] + \ldots \right\}. \tag{17}$$

In region I, at the same time, we have

$$\begin{aligned} \tilde{\Phi}(y) = 1 + \frac{y}{4p} + \frac{y+y^2}{(4p)^2} + \frac{4y + 2y^2 + y^3}{(4p)^3} + \ldots \\ \ldots + \lambda \left(F_1(y) + \frac{1}{4p} F_2(y) + \ldots \right) + \lambda^2 \left(Q_1(y) + \ldots \right) + \ldots , \end{aligned} \tag{18}$$

where

$$F_1(y) = \int_0^y \frac{e^t - 1}{t}\, dt + \gamma + \ln 4p; \qquad F_2(y) = (y-2)F_1(y) + 1 - y - e^y; \tag{19}$$

$$Q_1(y) = \int_0^y \frac{e^z}{z}\,dz \int_0^z dt\, e^{-t} F_1(t) + \frac{\pi^2}{12} + \frac{(\gamma + \ln 4p)^2}{2} - (\gamma + \ln 4p) F_1(y).$$

Finally, for A we obtain

$$A = A_0 + 4p\lambda \left(1 - \frac{4}{4p} - \frac{3}{(4p)^2} + \dots\right) - 4p(\gamma + \ln 4p)\lambda^2 + \dots \tag{20}$$

4. Knowing A, from (8) and (20) one can determine p, and thereby W and $\Delta W = W_u - W_g$. The resulting transcendental equation for p can be solved by expanding in a series in $1/R$. Then we obtain

$$p_{g,u} = \frac{R}{2} + \frac{1}{2} - \frac{1}{4R} + \frac{1}{4R^2} + \frac{13}{16R^3} + \dots \mp R^2 e^{-R-1}\left(1 - \frac{1}{2R} - \frac{1}{8R^2} + \dots\right)$$
$$- 2R^4 e^{-2R-2}(1 + \dots) + \dots; \tag{21}$$

$$W_{g,u} = -\frac{1}{2} - \frac{1}{R} - \frac{9}{4R^4} + \dots \mp 2Re^{-R-1}\left(1 + \frac{1}{2R} - \frac{25}{8R^2} + \dots\right)$$
$$+ 4R^3 e^{-2R-2}(1 + \dots) + \dots; \tag{22}$$

$$\Delta W = 4Re^{-R-1}\left(1 + \frac{1}{2R} - \frac{25}{8R^2} + \dots\right) + \dots \tag{23}$$

The method proposed above makes it possible, in principle, to obtain $X(\xi)$, $Y(\eta)$, and A with any prescribed accuracy. In this, the parameter in the corresponding expressions is $1/4p$, which even at $R = 2$, i.e., at the equilibrium distance between the nuclei, amounts to only $\sim 1/6$. At the same time, the expansion in $1/R$ in formulas (21)–(23) converges poorly at $R \sim 2$, so that it is meaningful to use it only for sufficiently large R; at $R \sim 2$, to find p, W, and ΔW, one must solve the transcendental equation for p numerically. It should be noted that formula (23) for ΔW gives results differing from the numerical values given in [4] by 0.1% at $R = 9$ and by 0.3% at $R = 4$.

There remains the question of the normalization of the functions obtained by us. In calculating the corresponding constant N^2, the integral over ξ is taken elementarily; to take the integral over η, the domain of integration must be divided into two parts: one domain from 0 to $(1 - \varepsilon/2p)$, and the other from $(1-\varepsilon/2p)$ to 1. In calculating the integral, the dependence on ε must disappear. As a result, for N^2 we obtain

$$N^2 = 2\pi \left(\frac{R}{2p}\right)^3 4^{\sigma-1} \left\{1 + \frac{3(\sigma+1)}{4p} + \frac{11\sigma^2 + 8\sigma + 11}{(4p)^2} + \dots\right.$$

$$... + 2\lambda \left[p + \left(\frac{\sigma - 3}{2} + 2\gamma + 2\ln 4p \right) + ... \right] + ... \Big\} . \quad (24)$$

The calculation of N^2 is an example of the calculation of the simplest matrix element with these functions.

5. It is not difficult to generalize the results obtained above both to the case of different Coulomb centers with arbitrary charge and to the case of other quantum numbers, which will be done subsequently. Moreover, in the case when the nuclear charges are greater than unity, the convergence of the corresponding series improves, while for higher quantum numbers the convergence will worsen. It is also of interest to calculate, with the functions given above, oscillator strengths and other matrix elements.

Physicochemical Institute
named after L. Ya. Karpov

Received
8 IV 1964

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Note: Figure translations are in progress. See original paper for figures.