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POLARIZATION OF THE HYDROGEN ATOM IN THE GROUND STATE BY THE FIELD OF A POINT CHARGE

V. P. SHMELEV

Moscow State University

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The dipole moment p of a hydrogen atom in the ground state, induced by a positive charge e, is considered as a function of the distance between the charge and the atomic nucleus (Fig. 2). The proton and the hydrogen atom in this state do not form a stable system. The stability of the proton-electron-positron quasimolecule is investigated with the aid of the solution thus obtained.

1. THE HYDROGEN ATOM IN THE FIELD OF A POINT CHARGE e

THE appearance of a dipole moment in the hydrogen atom is considered by us as a problem involving the motion of an electron in the field of two fixed positive charges e. Let the nucleus of the hydrogen atom a be fixed at the origin of the coordinate system, and let the charge e be at a point b a distance R along the z axis. We denote by r_a and r_b the respective distances from the electron to these points. It is now necessary to find a solution of the Schrödinger equation with potential

$$U_1 = -e^2/r_a - e^2/r_b,$$

which corresponds to the ground state of the hydrogen atom polarized by a charge e located at a distance R from it.

The given problem is solved by the same methods used for the well-known problem of two centers in the case of the hydrogen molecule. Only the boundary conditions change for $R \rightarrow \infty$; whereas the wave function of the ionized molecule of hydrogen changes, as $R \rightarrow \infty$, into a symmetric combination of hydrogen atoms at the points a and b, in our case the wave function goes over into a hydrogen atom with the nucleus at the point a. If we introduce the elliptic coordinates

$$\xi_0 = (r_a + r_b)/R, \qquad \eta_0 = (r_a - r_b)/R, \tag{1}$$

then we can separate the variables in the Schrödinger equation with potential U_1:

$$\Psi(r_a, r_b) = X(\xi_0)\,Y(\eta_0), \tag{2}$$

$$\frac{d}{d\xi_0}\left[(\xi_0^2 - 1)\frac{dX}{d\xi_0}\right] + [-\lambda^2\xi_0^2 + 2R\xi_0 + A]\,X = 0, \tag{2a}$$

$$\frac{d}{d\eta_0}\left[(\eta_0^2 - 1)\frac{dY}{d\eta_0}\right] + [-\lambda^2\eta_0^2 + A]\,Y = 0, \tag{2b}$$

where $\lambda = R\sqrt{|E|}/2$, while A denotes the separation constant.[1]

Here and below, the energy E is expressed in Rydbergs ($1\ \mathrm{Ry} = e^2/2a_0$), the distance R in Bohr radii, a_0, and the electron charge e is set equal to unity.

Let us fix the boundary conditions as $R \rightarrow \infty$. If the electron remains with the charge a, then upon removal of the point b to infinity along the z axis, the elliptical coordinates of (1) go over into parabolic coordinates

$$\xi_0 \rightarrow \mu/R + 1, \qquad \eta_0 \rightarrow \nu/R - 1,$$

where $\mu = r_a - z_a$, $\nu = r_a + z_a$. Equations (2a) and (2b) transform into the equations for a hydrogen atom at the point a in parabolic coordinates. In order that the solution $\Psi = X(\mu)\,Y(\nu)$, corresponding to the ground state of the hydrogen atom, exist for $R \rightarrow \infty$, it is necessary to require that

$$\lim_{R\rightarrow\infty} E(R) = -1 \quad \text{or} \quad \lim_{R\rightarrow\infty} \lambda(R) = R/2;$$

$$\lim_{R\rightarrow\infty} A(R) = |E|\,R^2/4 - R$$

$$= \lambda^2 - 2\lambda + b_0 + b_{-1}/\lambda + b_{-2}/\lambda^2 + \ldots$$

Then we get the limiting values for the functions X and Y at large R:

$$X(\xi_0) \approx C_1(R)\,e^{-\lambda\xi_0}, \qquad Y(\eta_0) \approx C_2(R)\,e^{-\lambda\eta_0}, \tag{3}$$

i.e., Ψ transforms into the function of an isolated hydrogen atom:

$$\lim_{R\rightarrow\infty} \Psi(\xi_0, \eta_0) = e^{-\lambda(\xi_0+\eta_0)} = e^{-r_a}.$$

For $R \rightarrow 0$, Eqs. (2) go over into the equation of a helium atom in spherical coordinates,[1] while the parameter A takes on one of the values $A = -l(l+1)$. For the ground state $l = 0$, we have

$A(0) = 0$. Such a definition of the limits for R equal to ∞ and 0 is based on the well-known theorem that, for an adiabatic change of the parameters of the system (R changes from ∞ to zero), the number of its quantum state (energy level) does not change.[2]

We now turn to Eqs. (2), which we shall solve under the boundary conditions (3). Both Eqs. (2a) and (2b) have the same characteristic equation relative to the singular points +1 and −1, one multiple root of which is $\rho = 0$. Consequently, for example at the point +1, each equation has one finite solution and one that is logarithmically divergent. The boundary conditions at the other point in each of the equations are different: $X(\xi_0)$ is bounded in the region $1 \leq \xi_0 < \infty$ and $Y(\eta_0)$ in the region $-1 \leq \eta_0 \leq +1$. The usual method of solution of Eqs. (2) is the following: initially, for a given λ, one finds a value of the parameter $A(\lambda)$ for which the mentioned solution $Y(\eta_0)$ exists [we note that Eq. (2b) does not depend explicitly on R]. When the parameter A is found as a function of λ, it is substituted in Eq. (2a), and then such an R is sought for which the solution $X(\xi_0)$ exists, bounded in the region $1 \leq \xi_0 \leq \infty$. The energy is then determined from the condition $\lambda^2 = -ER^2/4$.

Whereas only even or odd solutions of Eq. (2b) are obtained in the problem of the hydrogen molecule, $Y(\eta_0)$ in our case has no symmetry with respect to η_0. Therefore it is necessary to use the method of solution of the spheroidal equation (2b), developed by Wilson[3] for the general case. For this purpose, we make the substitution

$$Y(\eta_0) = e^{-\lambda\eta_0} y(\eta_0), \qquad x = r_0 - 1, \qquad \mu = A - \lambda(2 + \lambda)$$

in Eq. (2b). A solution that is finite at the point $x = 0$ ($\eta_0 = +1$) is sought in the form of a series

$$y(x) = \sum_{m=0}^{\infty} a_m x^m,$$

which leads to the recurrence relation

$$a_{m+1} = -u_m(\mu, \lambda, m)\, a_m + v_m(\mu, \lambda, m)\, a_{m-1}. \tag{4}$$

The eigenvalue μ is then determined from the condition that the solution must be finite at the other singular point $x = -2$ ($\eta_0 = -1$).

The coefficients a_m are determined from the infinite set of linear homogeneous equations (4), so that the vanishing of the determinant is necessary. It has been shown[3,4] that the condition of the vanishing of the infinite determinant of the system (4) is equivalent to the vanishing of the following infinite continued fraction:

$$0 = u_0 + \cfrac{v_1}{u_1 + \cfrac{v_2}{u_2 + \cfrac{v_3}{u_3 + \ldots}}}. \tag{5}$$

The elements of the continued fraction u_m and v_m are the coefficients of the system of equations (4), while $u_0 = \mu/2$. Wilson[3] proposed to find the values of $\mu_i(\lambda)$ for which the solutions $Y(\eta_0)$ exist, bounded at the point $\eta_0 = -1$, as roots of Eq. (5). This is possible only in the case of the convergence of the infinite continued fraction (5). The fraction converges[4,3] in the case when just those roots of $\mu_i(\lambda)$ of the equation $\Delta(1, u_m, -v_m) = 0$ which correspond to the indicated solutions $Y(\eta_0)$ are substituted in the functions $u_m(\mu, \lambda, m)$ and $v_m(\mu, \lambda, m)$.

We shall seek the root $\mu(\lambda)$ which vanishes for $\lambda = 0$. It corresponds to a state with the lowest energy level.[1] In the case of small λ, we can find for it a power series in λ by making use of the method of successive approximations suggested by Wilson:[3]

$$\mu = -2\lambda - \frac{2}{3}\lambda^2 + \frac{4^3}{3 \cdot 5^3}\lambda^4 + \ldots$$

Then the following series holds for $A(\lambda)$ in the case of small λ:

$$A(\lambda) = \frac{1}{3}\lambda^2 + \frac{4^3}{3 \cdot 5^3}\lambda^4 + \frac{4^4}{3^4 \cdot 5^4}\lambda^5 + \ldots \tag{6}$$

For λ → 0, the function $A(\lambda)$ coincides with the same parameter for the hydrogen molecule;[3] there, the series contains only even powers of λ, and the first term is $\lambda^2/3$.

The values of the root $\mu(\lambda)$ for large λ are found from the finite continued fraction made up of the first few elements u_m and v_m. Their number is larger the larger the value of λ. To calculate the continued fraction, it is convenient to use the results set forth in the monograph by Perron;[4] the fraction (5) is classified as "limiting periodic."

After finding the values of A for a number of values of λ, we find the value of R for each pair of numbers A and λ as eigenvalues of (2a). Teller[1] suggested a variational principle for this problem, in which the test function $X(\xi_0) = \exp(-\lambda\xi_0)$ is a sufficiently good approximation. In the problem for the conditional extremum

$$\delta I = \delta \int_1^{\infty} \{(\xi_0^2 - 1) X'^2 + (\lambda^2\xi_0^2 - A) X^2\}\, d\xi_0, \qquad \int_1^{0} 2\xi_0 X^2 d\xi_0 = 1$$

the quantity R is a Lagrange multiplier, which is found from the condition

$$R = \min \left\{ I \Big/ \int_1^\infty 2\xi_0 X^2 d\xi_0 \right\}.$$

It is useful to write the wave function $Y(\eta_0)$ in the form

$$Y(\eta_0) = e^{-\lambda\eta_0}(a_0 + a_1\eta_0 + a_2\eta_0^2 + \ldots) \approx e^{-\gamma\eta_0},$$

where $\gamma(R) = \lambda(R) - \delta(R)$, $\lim_{R\to\infty} \delta = 0$. Then $\gamma(R)$ is determined from the condition of the minimum of the functional

$$S(\gamma) = \int_{-1}^{+1} \{(\eta_0^2 - 1) Y'^2 + (\lambda^2\eta_0^2 - A) Y^2\} \, d\eta_0.$$

Since $A(\lambda)$ is already determined, this is a problem of an absolute extremum. For large λ, the derivative $dS/d\gamma$ vanishes if $A = \lambda^2 - 2\lambda + 1$ (here, $\gamma = \lambda$). The condition $\delta S = 0$ is satisfied for small λ also, if $A(\lambda)$ is taken from the series (6). Such a simplified expression

$$\Psi(\xi_0, \eta_0) = \exp(-\lambda\xi_0 - \gamma\eta_0)$$

is similar to the wave function of the ionized hydrogen molecule obtained by Guillemin and Zener,[5] also from a variational principle. For large R, it is convenient to write it in the form $\Psi = e^{-r_a} e^{\delta\eta_0}$. The result is that the spherically symmetric electron shell of the hydrogen atom is somewhat elongated in the direction of large η_0, i.e., toward the charge $+e$.

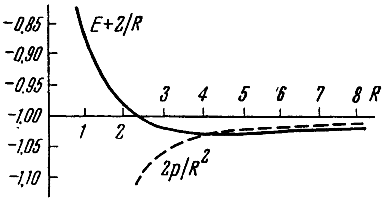

FIG. 1

The solid line in Fig. 1 gives the curve of the electron energy $E = -4\lambda^2/R^2$ combined with the energy of separation of the charge e from the nucleus of the atom, i.e., the energy $E + 2/R$. The resultant curve does not form a deep potential well; its maximum depth of 0.03 is reached for $R = 4$; the system goes over into the much deeper level of the hydrogen molecule only if the proton is entirely removed from the atom.

In order to find the dipole moment of the hydrogen atom induced by the charge e, we write down the normalized function Ψ. Here it is convenient to use the coordinates

$$\xi = \xi_0 R = r_a + r_b, \qquad \eta = \eta_0 R = r_a - r_b \tag{7}$$

and introduce the notation used in reference 5:

$$\alpha = 2\lambda / R, \qquad \beta = 2\gamma / R.$$

Normalization of the wave function depends on R:

$$\Psi(\xi, \eta) = C(R) f(R, \xi, \eta),$$
$$f(R, \xi, \eta) = \exp(-\alpha\xi/2 - \beta\eta/2). \tag{8}$$

The condition of normalization in the coordinates (7) has the form

$$\tfrac{1}{4}\pi C^2(R) J(R) = 1, \qquad J(R) = \frac{1}{R}\int_R^\infty d\xi \int_{-R}^{+R} d\eta \, (\xi^2 - \eta^2) f^2. \tag{9}$$

The function $J(R)$ increases monotonically from $J(0) = \frac{1}{2}$ to $J(\infty) = 4$. Then Eq. (9) determines the normalizing factor $C(R)$. The dipole moment of the hydrogen atom in the state (8) is determined as

$$-p = \frac{\pi C^2}{4R} \iint r_a \cos\theta \, (\xi^2 - \eta^2) f^2 \, d\xi \, d\eta,$$

where θ is the angle between r_a and R. Integrating over $d\xi$ and $d\eta$, we get the dipole moment $p(R)$ as a function of the distance between the charge e and the nucleus of the atom. From the graph of $p(R)$ in Fig. 2, it is seen that this dipole moment is a short-range effect. In Fig. 1, the broken line shows the energy of interaction of the dipole p and the charge e, equal to $2p/R^2$. Beginning with $R = 4$, this energy is very close to the curve $E + 2/R$.

2. STABILITY OF THE PROTON-ELECTRON-POSITRON QUASIMOLECULE

By using the given solution, we shall try to find such a state of the proton, electron and positron system (pe^-e^+), which should dissociate into a positron and a hydrogen atom. For this purpose, we use the variational method employed earlier by the author[6] for the calculation of such a state of the system (pe^-e^+), which dissociates into a proton and a positronium atom: $p + (e^+e^-)$. Here also, the system is treated in the adiabatic approximation, with a fixed positron, but now its state is determined by the wave function (8), and not by the function of the hydrogen molecule. We seek a wave function of the system (pe^-e^+) in the form

$$\psi(r, \xi, \eta) = \Phi(r) F(r, \xi, \eta), \tag{10}$$

where $F(r, \xi, \eta)$ corresponds to the function $\Psi(\xi, \eta)$, which is determined by means of (8),

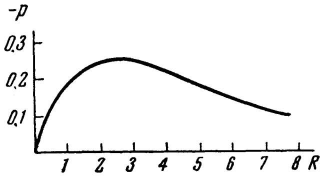

FIG. 2

only the parameter R is replaced by the variable r — the coordinate of the positron. The function $F(r, \xi, \eta)$ is normalized to unity in the coordinates ξ, η, as is shown in (9). The wave function of the positron, $\Phi(r)$, remains arbitrary; its value must be determined from the condition of the minimum of the functional

$$S = \iiint L\left(r, \xi, \eta, \frac{\partial\psi}{\partial r}, \frac{\partial\psi}{\partial\xi}, \frac{\partial\psi}{\partial\eta}, \psi\right) d\tau,$$

where the Lagrangian function of the system (pe^-e^+) and the element of volume $d\tau$ in the coordinates r, ξ, η are given in reference 6. Substituting the function (10) in this integral, and integrating over the coordinates ξ and η, we arrive at the isoperimetric variational problem

$$\delta S = \delta \int_0^\infty \left(\frac{d\Phi^*}{dr}\frac{d\Phi}{dr} + U(r)\,\Phi^*\Phi\right) r^2\,dr, \quad \int_0^\infty \Phi^*\Phi r^2\,dr = 1 \tag{11}$$

by the same means as previously.[6] Here, the potential $U(r)$ is a function of r, expressed both directly in terms of r and also by $\alpha(r)$ and $\beta(r)$;

$$\begin{aligned} U(r) = {} & \left(\frac{2}{r} + \frac{\alpha^2 + 5\beta^2 - 2\alpha\beta}{4}\right) + \frac{1}{4rJ}\left(\frac{d\alpha}{dr}\frac{\partial}{\partial\alpha} + \frac{d\beta}{dr}\frac{\partial}{\partial\beta}\right)^2 (rJ) \\ & - \left(\frac{1}{2J}\frac{dJ}{dr}\right)^2 + \frac{8}{rJ}\frac{e^{-\alpha r}}{\alpha\beta}\left\{\left(r + \frac{1}{\alpha}\right)\left(\frac{\alpha^2 - \beta^2}{2\alpha} - 2\right)\sinh\beta r\right. \\ & + \frac{\alpha - \beta}{4}\left[\frac{d\alpha}{dr}\left(\frac{r^2}{\alpha} + \frac{3r}{\alpha^2} + \frac{3}{\alpha^3} + \frac{r^2}{2\beta} + \frac{r}{\alpha\beta} + \frac{1}{\alpha^2\beta}\right)\right. \\ & \times \left(\cosh\beta r - \frac{\sinh\beta r}{\beta r}\right) + \frac{d\beta}{dr}\left(r + \frac{1}{\alpha}\right)\left[\left(\frac{2}{\alpha\beta} + \frac{3}{\beta^2}\right)\right. \\ & \left.\left.\left.\times \left(\cosh\beta r - \frac{\sinh\beta r}{\beta r}\right) - \left(\frac{r}{\alpha} + \frac{r}{\beta}\right)\sinh\beta r\right]\right]\right\}. \end{aligned} \tag{12}$$

The function $J(R)$ is determined by Eq. (9). For $r \to 0$, the potential $U(r)$ increases according to Coulomb's law. Taking it into account that $\alpha(\infty) = \beta(\infty) = 1$, we find the limit at infinity:

$$\lim_{r\to\infty} U = -1,$$

toward which $U(r)$ tends according to the exponential law re^{-br}.

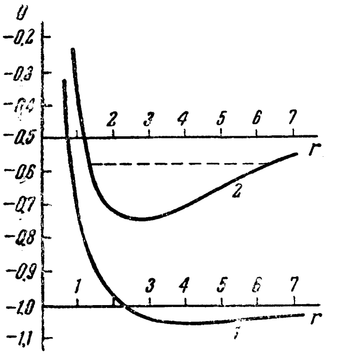

FIG. 3

The variational problem (11) corresponds to the Schrödinger equation with the potential energy (12), and its Lagrangian multiplier corresponds to the eigenvalue of the energy E_n. The potential (12) is plotted in Fig. 3 (curve 1). The maximum depth of $U(r)$ is equal to -1.05 and is reached at $r = 4$. However, the "free energy" amounts to -0.05. In the same drawing, we have plotted the curve (term) for the state of the system (pe^-p^+) which we found earlier (curve 2), which dissociates into a proton and a positronium atom.[6] This curve has the limit $-\frac{1}{2}$ for $r \to \infty$, and a depth of the potential well equal to -0.26. The depth of the potential well, -0.05, of the new term (12) is insufficient for the existence of stationary states of positronium. All attempts at changing $\alpha(r)$ and $\beta(r)$ arbitrarily (variation) have failed to make any appreciable increase in this depth. Therefore, although the application of the variational principle still does not prove the absence of stationary states, it is nevertheless very probable that there are none. The positron could be kept in the potential well (12) if its mass were four times greater. In order to find the energy of the system (pe^-e^+), Ore[7] took the wave function of the ionized hydrogen molecule H_2^+, and then decreased the mass of one of its protons. By a variational method, he found that this system would exist had the mass of the proton amounted to 4.5 m (m = mass of electron). The results obtained by us furnish a basis for assuming that this result of Ore is final. Thus, it is necessary to regard the lowest state of the system (pe^-e^+) as the state found earlier[7] with energy $E = -0.563$. This state is stable, inasmuch as the new term (12) does not overlap the first, i.e., there is no predissociation.

In conclusion, the author expresses his deep gratitude to his supervisor, Prof. A. A. Sokolov, and also to Prof. V. I. Gol'danskiĭ.

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