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DETERMINATION OF THE ENERGY OF INTERACTION BETWEEN ATOMIC POSITRONIUM AND MOLECULES OF THE MEDIUM

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The possibility of determining the magnitude of the energy of interaction between the hydrogen-like positronium atom and molecules (atoms) of the surrounding medium is considered on the basis of spectroscopic data on the energy level shifts. The proposed method is also used to describe the hyperfine structure level shifts in other atoms such as tritium, muonium etc. The magnitudes of the interactions mentioned are determined by taking into account the available experimental data. The method is used with the aim of verifying for describing the Stark effect of the hydrogen-atom ground state.

CALCULATION of the interatomic (intermolecular) interactions is of considerable interest, owing to the lack of methods for their direct measurement.

However, even in the calculation of the interaction between two simplest isolated atoms, it becomes necessary to confine oneself to crude approximations. On the other hand, the calculation of the interaction energy of a system consisting of three atoms is one of the most difficult problems. The mathematical difficulties encountered in attempts to solve the problem of interaction of an individual atom with a system containing an arbitrary number of molecules (atoms) and in the solid, liquid, or gaseous state, are therefore obvious.

For example, the calculated binding energy of isolated hydrogen atoms (H) and positonium (Ps) in the (PsH) molecule is subject, as noted in[1,2], to a considerable uncertainty. The question of the influence of pressure and temperature on the binding energy of such associated states is still unsolved.

Furthermore, a hypothesis has already been advanced concerning the possible formation of an intermediate complex of atomic positronium surrounded by the molecules of the medium, particularly the formation of an intermediate complex with an acceptor of the PsAc type[3], and moreover the possibility of solvatation of the Ps atom itself in an aqueous solution was indicated[4]. However, the value of the binding energy of the Ps atom with its surrounding molecules of the medium in the intermediate complexes and in the solvated states, if such states exist, still remains unknown. The influence of temperature on the stability of such bound states is unclear. At the same time, a shift of the levels of the hyperfine structure of the Ps atom in water there was observed in a number of investigations[5,6]. This phenomenon has not yet been explained. In addition, a shift of the levels of the hyperfine structure of a positonium atom as a function of the pressure of the surrounding gas was observed in[7], and likewise found no explanation.

The purpose of this communication is to point to the possibility of determining the interaction between an atom (to the specific, a positronium atom) and the molecules of the medium surrounding it on the basis of spectroscopic data on the shift of the energy levels of the atom in the medium, and to obtain numerical values for the indicated interactions. It is assumed here that the Ps atom does not lose its main properties as the result of such interactions (e.g., no ionization of the Ps atom takes place).

Let us assume that the positronium atom is located in some medium that is neutral to it. Since it is subject to an additional interaction of the molecules (atoms) surrounding it, compared with vacuum, there is superimposed on the electromagnetic interaction between the electron and the positron of the Ps atom also an interaction with the medium that is external with respect to this atom; this is equivalent to the presence of an effective field E. We shall assume the quantity $\partial\mathscr{E}/\partial r$ to be constant at distances on the order of the dimensions of the Ps atom itself. (This limitation is not significant, and is introduced for the purpose of simplification. Introduction of terms containing $\partial^n\mathscr{E}/\partial r^n$ can in principle increase the accuracy of the derivations presented below.)

The Schrödinger equation for atomic positronium under the aforementioned conditions can be written in the form

$$(H-E)\psi=0, \tag{1}$$

where

$$-H=\frac{\hbar^2}{m}\Delta+\frac{e^2}{r}+\zeta e\mathscr{E}(r-3a)-\zeta e\frac{\partial\mathscr{E}}{\partial r}(r^2-12a^2). \tag{1a}$$

Here $\hbar = \hbar/2\pi$ and h is Planck's constant,

$$\Delta=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right),$$

e is the electron charge, r is the instantaneous distance between the electron and the positron of the Ps atom, ζ is a parameter that takes into account the deformation of the electron cloud of the Ps atom by the medium, $3a = \langle\psi(1s)|r|\psi(1s)\rangle$, $12a^2 = \langle\psi(1s)|r^2|\psi(1s)\rangle$, $\psi(1s)$ is the wave function of the ground state of the isolated positronium atom, normalized to unity, 2a is the radius of the first Bohr orbit of the Ps atom, and m is the electron mass.

Substituting in (1a) $\partial\mathscr{E}/\partial r = A$ and $\mathscr{E} = Ar + B$, where A and B are constants, we get

$$-H=\frac{\hbar^2}{m}\Delta+\frac{e^2}{r}+\zeta e(Ar^2+Br-3aAr-3aB)-\zeta eA(r^2-12a^2). \qquad (2)$$

The solution of Eq. (1) with allowance for (2) is sought in a class of wave functions of the form

$$\psi=\exp(-\zeta r/2a). \qquad (3)$$

Substituting (3) in (2), we get

$$\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}=\frac{\zeta^2e^2}{4a}-\frac{\zeta e^2}{2a}-3eaB+9a^2Ae+3\zeta eaB-12a^2eA\zeta, \qquad (4)$$

with $\langle\psi|\psi\rangle = 8\pi a^3\zeta^{-3}$. Starting from the stationarity condition $\langle\psi|H|\psi\rangle/\langle\psi|\psi\rangle$, we obtain

$$\frac{\zeta e^2}{2a}-\frac{e^2}{2a}+3aeB-12a^2eA=0 \qquad (5)$$

and finally

$$\zeta=1-\frac{6a^2B}{e}+\frac{24a^3A}{e}. \qquad (6)$$

In this case the wave function, normalized to unity, of the Ps atom of the ground state of the deformed 1s wave in the field of the medium takes the form

$$\psi=\zeta^{3/2}(8\pi a^3)^{-1/2}\exp\left(-\frac{\zeta r}{2a}\right). \qquad (7)$$

The excess of energy of the triplet over the singlet for the positronium atom for the indicated wave function (7), is

$$\nu=\nu_0\left(1-\frac{6a^2B}{e}+24\frac{a^3A}{e}\right)^3, \qquad (8)$$

where $h\nu_0$ is the excess of the energy of the triplet over the singlet in vacuum.

Since the level shift of the hyperfine structure of the Ps atom in the medium is a consequence of the process of the action exerted on the positronium atom by all the internal fields of the medium, which differ in structure and in character[8], we shall start with the Gell-Mann-Feynman theory[9] and confine ourselves in the calculation of the energy of the interaction between the Ps atom and the medium to the value of a constant and uniform effective field $\mathscr{E}$ such that its action on the Ps atom is equivalent to the vector sum of the fields of the medium acting on the atomic positronium. In such a case, the term $\zeta e\mathscr{E}(r-3a)$ in (1a), which describes the action of the medium, can be transformed, by substituting the value of ψ from (3) in expression (2) and dividing by $\langle\psi|\psi\rangle$, into

$$U=-3ae\mathscr{E}(1-\zeta). \qquad (9)$$

Substituting (6) in (9) with allowance for the fact that $A = 0$ and $B = \mathscr{E}$, we readily obtain an expression for the interaction energy of the positronium atom with the field $\mathscr{E}$:

$$U=-3ae\mathscr{E}(1-\zeta)=-18a^3\mathscr{E}^2. \qquad (10)$$

Using spectroscopic data on the level shift of the hyperfine structure of the atomic positronium in the medium and expression (8) where $A = 0$, we obtain the value of the effective field $\mathscr{E}$. Substituting the obtained expression $\mathscr{E}$ in (10), we obtain the value of the interaction energy between the Ps atom and the medium surrounding it.

Carrying out such a procedure for the case of finding the Ps atom in water, we have $U_1 = -4.1 \times 10^{-14}$ erg and $U_2 = -1.7 \times 10^{-13}$ erg respectively for $h\nu_1 = 7.30 \times 10^{-4}$ eV and $h\nu_2 = 6.32 \times 10^{-4}$ eV from the data of[5]; $U_3 = -5.3 \times 10^{-13}$ erg for $h\nu_3 = 5.00 \times 10^{-4}$ eV in accordance with the data of[6], and finally, according to[6,10], $U_4 = -1.8 \times 10^{-12}$ erg for $h\nu_4 = 3 \times 10^{-4}$ eV.

For the excess energy of the triplet over the singlet of the positronium atom in vacuum we assume in the foregoing calculations and subsequently the value $h\nu_0 = 8.34 \times 10^{-4}$ eV.

Although the foregoing numerical values were obtained on the basis of experimental quantities that deviate somewhat from one another, nonetheless they confirm the hypothesis that there exists a bound state (or bound states) of atomic positronium in water at room temperatures.

Let us approximate the expressions given above for the case of atomic positronium located in a real gaseous medium. Under the concrete conditions realized in[7], we can neglect the proper volume occupied by the gas molecules, compared with the volume in which they are situated. In this case $\partial\mathscr{E}/\partial r = 0$, and expression (8) is written in the form

$$\nu=\nu_0(1-6a^2\mathscr{E}/e)^3. \qquad (11)$$

Carrying out concrete calculations on the basis of the available data on the level shift of the hyperfine structure of atomic positronium[7], in accord with (11), we can verify that $|6a^2\mathscr{E}/e| \ll 1$, and in addition, on the basis of (10) we can verify that $|U| \ll kT$ at $T = 300^\circ$K. When this is taken into account, expression (11) is easily transformed, owing to the smallness of the second term, into

$$\nu=\nu_0(1-18a^2\mathscr{E}/e). \qquad (12)$$

Let us apply expression (12) to the data of[7], so as to derive an expression for the level shift of the hyperfine structure of atomic positronium as a function of the pressure of the surrounding gas. The potential energy of the interaction between the positronium atoms and argon is taken in the "6–12" Lennard-Jones form[9]:

$$U=4\varepsilon\left[\left(\frac{\sigma}{R}\right)^{12}-\left(\frac{\sigma}{R}\right)^{6}\right]. \qquad (13)$$

Here σ and ϵ are constants defined in greater detail in[9]; R is the average distance between atoms. For not too high pressures it is possible to neglect, with very slight error, the first term of expression (13). Combining (10) and (13) under these conditions, we readily obtain

$$\mathscr{E}=\pm\frac{c'}{R^3}, \quad c'=\left(\frac{2\varepsilon\sigma^6}{9a^3}\right)^{1/2}. \qquad (14)$$

When $|U| \ll kT$, the gas pressure is $P = 3kT/4\pi R^3$. Generally speaking, the criterion that should be used here is not the energy of interaction between the positronium atom and the argon atoms, but the energy of the interaction between the argon atoms. However, since the atomic positronium is assumed to be a free radical[4], we can expect for the energy of interaction between the inert-gas atoms only a lower value of interaction than between the positronium atom and the argon atoms, and consequently we can expect only a strengthening of the inequality $|U| \ll kT$ at $T = 300°K$.

The foregoing argument is not unique. We can verify by direct calculation on the basis of[9] that, independently of the reasoning advanced here and in[4], the inequality $|U| \ll kT$ holds at $T = 300°K$ for the interaction energy between the inert-gas atoms at not too high pressures. Starting from (14), we obtain

$$\mathscr{E} = \pm D'P, \tag{15}$$

where $D' = 3kT/4\pi c'$. Substituting the value of $\mathscr{E}$ from (15) in (12), we get

$$\nu = \nu_0(1 \pm DP), \tag{16}$$

where $D = 18a^2D'/e$.

The linear relation obtained in (16) between the level shift of the hyperfine structure of atomic positronium and the pressure is a reflection of the linear dependence resulting from the data of the precision experiment in[7].

Since the expression for D contains the parameters of the Lennard-Jones potential, it follows that by using the experimental value of D it is possible to obtain, subject to some additional condition, the parameters ϵ and σ for atomic positronium in gaseous argon.

Following a procedure analogous to that described for finding the interaction energy between the Ps atom and water, we find for the case when positronium is in gaseous argon at room temperature, on the basis of the data of[7], that the atomic positronium can associate with argon, but the energy of their interaction at $T = 2 \times 10^3$ Torr is $U = -8.3 \times 10^{-20}$ erg, i.e., much less than the thermal energy.

The foregoing reasoning and calculation method can be extended in trivial fashion to include also other hydrogenlike atoms: muonium, deuterium, hydrogen, etc., leading to agreement with the data obtained by precision experiments[11-15].

As a check, let us apply the foregoing method to the study of the behavior of the ground state of the hydrogen atom in a homogeneous external electric field $\mathscr{E}$. In analogy with (1) and (1a), we write the Schrodinger equation in the form

$$(H - E)\psi = 0, \tag{17}$$

$$-H = \frac{\hbar^2}{2m}\Delta + \frac{e^2}{r} + \zeta e\mathscr{E}(r - 1.5a). \tag{17a}$$

The notation is the same here as in (1) and (1a), and in addition, $1.5a = \langle \psi(1s) | r | \psi(1s) \rangle$, where $\psi(1s)$ is the wave function of the ground state of the isolated hydrogen atom, normalized to unity. The solution of Eq. (17) with allowance for (17a) is sought in a class of functions of the type

$$\psi = \exp(-\zeta r/a). \tag{18}$$

Taking (18) into account, we get

$$\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\zeta^2 e^2}{2a} - \frac{\zeta e^2}{a} - 1{,}5ae\mathscr{E}(1 - \zeta), \tag{19}$$

where $\langle \psi | \psi \rangle = \pi a^3 \zeta^{-3}$. With allowance for the stationarity of expression (19), we readily obtain

$$\zeta = 1 - 1{,}5a^2\mathscr{E}/e \tag{20}$$

with

$$U = -1{,}5ae\mathscr{E}(1 - \zeta) = -2{,}25a^3\mathscr{E}^2. \tag{21}$$

The values of the dipole moment of the polarizability of the hydrogen atom of the ground state are respectively $2.25a^3\mathscr{E}$ and $4.5a^3$. The obtained values are in full agreement with the available experimental data[9], and also with Stark-effect calculations by perturbation theory.

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