The compressed hydrogen atom

Staffan Yngve

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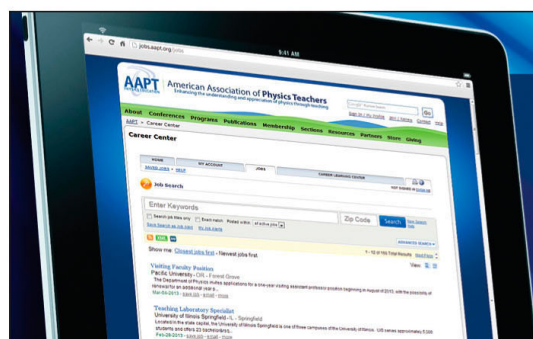
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The compressed hydrogen atom

Staffan Yngve

Institute of Theoretical Physics, Thunbergsvägen 3, S-752 38 Uppsala, Sweden

A simple model of a compressed hydrogen atom and an approximate formula for the energy shift due to compression are presented. The model is used in a theoretical lab, where the numerical energy shifts obtained from the approximate formula are compared with the results of an independent numerical calculation starting from the radial Schrödinger equation with boundary conditions.

I. INTRODUCTION

The radial Schrödinger equation for the relative motion of the electron and the proton in a free, uncompressed hydrogen atom with boundary conditions $u(0) = u(\infty) = 0$ is exactly soluble, the solution being a textbook example. If, however, the hydrogen atom is enclosed in an impenetrable sphere of radius a ("compressed hydrogen atom"), the boundary conditions are $u(0) = u(a) = 0$. This change of boundary condition causes an upward shift of every energy level, which cannot be studied without using some approximation.

The wavefunctions for the states of the compressed hydrogen atom cannot be simply expressed in terms of the eigenfunctions of the free hydrogen atom since the two problems correspond to different boundary conditions. Hence, the Rayleigh–Schrödinger perturbation theory does not apply.

An other approximation method is the WKB method. One standard illustration of the WKB method is the symmetric double-well potential, originally treated by Dennison and Uhlenbeck.[1] As pointed out by Fröman,[2] the usual WKB treatment of the double-well potential is not satisfactory, since the one-directional nature of the connection formulas[3,4] has been disregarded. In Ref. 2 the quantization condition for the double oscillator is derived by the method developed by Fröman and Fröman[4] for the rigorous solution of the connection problems. For energies below the top of the barrier, the particle should classically only be able to move in either of the two wells, but due to quantum mechanical tunneling, we obtain a correction to the single-well quantization condition taking only the classical motion into account.

The Dennison–Uhlenbeck quantization condition[1] for the symmetric double oscillator [see Eq. (3) in Sec. II] contains an exponential correction, due to quantum mechanical tunneling, and this correction is often smaller than the error in the quantization condition itself. The re-sults have however proved to account fairly well for the energy splitting of the energy levels.[2]

We now observe that the odd-parity wavefunction of the symmetric double oscillator has the same properties as the wavefunction of a compressed simple oscillator with an impenetrable wall at a point corresponding to the point of symmetry for the double-well potential. In Sec. III we use this analogy to guess what the quantization condition of a compressed atom should look like. The result is in agreement with the result of a rigorous treatment[5] of the problem of obtaining the energy shift due to compression based on the method for handling the connection problem developed by Fröman and Fröman.[4] The rigorous solution gives an analytical expression for the energy shift.

In a theoretical lab at our institute, the analytical formula for the energy shift of the hydrogen atom due to compression is compared with the result of a brute-force numerical calculation using a second-order difference approximation in the radial Schrödinger equation. The exercise can be performed in any course of quantum mechanics, where the students are familiar with the Bohr–Sommerfeld quantization and the quantum theory of the hydrogen atom. Although we have used a VAX computer the program can be implemented on a personal computer.

II. THE SEMICLASSICAL QUANTIZATION CONDITION FOR A SINGLE-WELL AND A SYMMETRIC DOUBLE-WELL POTENTIAL

For a particle with mass m, which moves with energy E_n in a real potential $V(x)$, the semiclassical momentum p_x is defined by

$$p_x^2/(2m) = E_n - V(x). \tag{1}$$

Let us first consider a single-well potential. According to the Bohr–Sommerfeld quantization rule[3] if p_x is integrated over a cycle of motion from one classical turning point (for

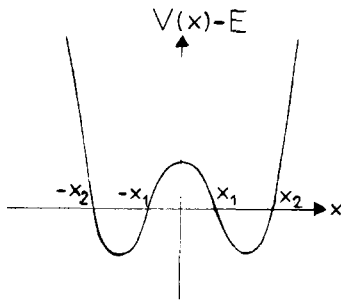© 1986 American Association of Physics Teachers   1103

Fig. 1. Qualitative behavior of $V(x) - E$ for a double oscillator.

which $p_x = 0$) to another and back, the result should be $(n + \frac{1}{2})h$, where h is Planck's constant. Hence

$$2\int_{x_1}^{x_2} \{2m[E_n - V(x)]\}^{1/2} dx = (n + \frac{1}{2})h, \quad n = 0,1,2,\ldots ,$$
(2)

where x_1 and x_2 denote the classical turning points. It is easy to show (cf. Ref. 3) that the quantization rule (2) gives the energy levels of the linear harmonic oscillator correctly.

Consider now a symmetric double oscillator (Fig. 1) with four classical turning points $-x_2, -x_1, x_1, x_2$. This problem was originally considered by Dennison and Uhlenbeck[1] for energy levels lying well below the top of the barrier. For a rigorous treatment of the double oscillator see Ref. 2. Dennison and Uhlenbeck[1] used the (first-order) WKB approximation for obtaining the energy levels, although the derivation of the formulas is not satisfactory, since the one-directional nature of the connection formulas[3,4] has been disregarded. The Dennison and Uhlenbeck quantization condition for the symmetric double oscillator reads

$$2\int_{x_1}^{x_2} \{2m[E_n - V(x)]\}^{1/2} dx \pm \frac{h}{\pi} \arctan\left(\frac{1}{2}e^{-2K}\right)$$
$$= (n + \frac{1}{2})h, \quad n = 0,1,2,\ldots ,$$
(3)

where

$$K = \frac{2\pi}{h}\int_0^{x_1} \{2m[V(x) - E_n]\}^{1/2} dx,$$
(4)

and where the upper sign in (3) corresponds to even-parity states and the lower sign in (3) to odd-parity states. The symmetric double oscillator as compared to the "corresponding single oscillator with classical turning points x_1 and x_2" is an important example of quantum mechanical tunneling, the effect of which cannot be neglected if effects of the order e^{-2K} are of interest. The effect due to tunneling is often smaller than the error in the quantization condition. However, formula (3) with (4) is sufficiently accurate to calculate, for example, the energy splitting between the odd parity state and the even parity state with the same n.

III. THE SEMICLASSICAL QUANTIZATION CONDITION FOR A FREE ATOM AND A COMPRESSED ATOM

Let us consider an electron with mass m, which moves in a real central potential $V(r)$ with the energy E_n and the angular momentum value L, the energy and the angular

momentum being constants of the motion. We saw for the single-well case that if the semiclassical momentum is integrated over a cycle of motion, the result equals the Planck's constant multiplied by a positive half-integral number. Let us now assume that the same relation holds for the (semiclassical) angular momentum integrated over one period of the corresponding variable, the angle φ, from 0 to 2π. Since L is constant, we obtain

$$L = (l + \frac{1}{2})\hbar, \quad l = 0,1,2,\ldots .$$
(5)

In quantum mechanics

$$L = [l(l+1)]^{1/2}\hbar = (l + \frac{1}{2})[1 - \frac{1}{4}/(l + \frac{1}{2})^2]^{1/2}\hbar$$
$$\approx (l + \frac{1}{2})\hbar,$$

for large l, and in the semiclassical calculations we shall use the value $(l + \frac{1}{2})\hbar$ of L.

In classical mechanics use is made of the identity

$$L^2 = (\mathbf{r} \times \mathbf{p}) \cdot (\mathbf{r} \times \mathbf{p}) = r^2 p^2 - (\mathbf{r} \cdot \mathbf{p})^2 = r^2 p^2 - r^2 p_r^2,$$
(6)

where $\mathbf{r}$ is the position vector and $\mathbf{p}$ is the momentum vector; p_r is the radial momentum. Using (5), (6) and the relation $E_n = p^2/(2m) + V(r)$, we have

$$p_r^2 = 2m[E_n - V(r)] - (l + \frac{1}{2})^2 \hbar/r^2$$
(7)

for the semiclassical radial momentum. The classical turning points are those values of r (> 0) for which $p_r = 0$, and we shall now assume that there are two classical turning points r_1 and r_2, where $r_1 < r_2$.

If p_r is integrated over a cycle of motion from r_1 to r_2 and back, the result should be $(k + \frac{1}{2})2\pi\hbar$, where k is a nonnegative integer. Hence, according to (7) we have the quantization condition originally obtained by Kramers[6]:

$$2\int_{r_1}^{r_2} \left\{2m[E_n - V(r)] - \left(l + \frac{1}{2}\right)^2 \hbar^2/r^2\right\}^{1/2} dr$$
$$= (k + \frac{1}{2})2\pi\hbar, \quad k = 0,1,2,\ldots ,$$
(8)

where

$$n = k + l + 1.$$
(9)

Note, that the energy eigenvalues obtained from (8) in general also depend on l.

For the hydrogen atom with

$$V(r) = -\hbar^2/ma_0 r,$$
(10)

($a_0 =$ the Bohr radius), the integral on the left of (8) gives

$$\int_{r_1}^{r_2} \left[2m\left(E_n + \frac{\hbar^2}{ma_0 r}\right) - \frac{(l + \frac{1}{2})^2 \hbar^2}{r^2}\right]^{1/2} dr$$
$$= \frac{\hbar^2 \pi}{a_0(-2mE_n)^{1/2}} - \left(l + \frac{1}{2}\right)\hbar\pi.$$
(11)

With (9), (8), and (11) give

$$(-2mE_n)^{1/2} = \hbar/a_0 n,$$
(12)

or

$$E_n = -\frac{\hbar^2}{2ma_0^2 n^2}, \quad \begin{array}{l} n = k + l + 1, \\ k = 0,1,2,\ldots, \\ l = 0,1,2,\ldots . \end{array}$$
(13)

Equation (13) is the well-known formula for the energy levels of the hydrogen atom. The same energy levels are obtained by solving the radial Schrödinger equation together with the boundary conditions that the radial wave-
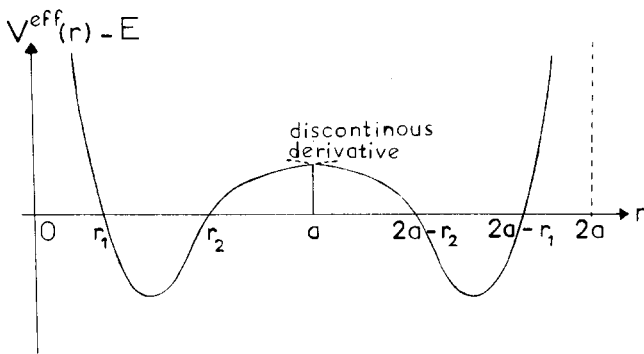
Fig. 2. The double oscillator constructed by reflecting the effective potential function (less E) on the interval $0 < r < a$ in the vertical line $r = a$. The dashed lines near $r = a$ indicate the discontinuous derivative of the double-well potential at $r = a$.

function shall vanish for $r = 0$ and in the limit as r tends to infinity.

We now introduce a simple model of an atom exposed to a high pressure (e.g., inside a star). We assume that the electron is enclosed in a large sphere of radius $a > r_2$ with impenetrable walls. The usual boundary condition for the free atom at infinity is then replaced by the boundary condition that the radial wavefunction should vanish for $r = a$. To obtain an approximate solution of this problem let us consider an effective double oscillator potential (cf. Fig. 2)

$$V^{\text{eff}}(r)$$

$$= \begin{cases} V(r) + (l + \tfrac{1}{2})^2 \hbar^2 / 2mr^2, & 0 < r < a \\ V(2a - r) + (l + \tfrac{1}{2})^2 \hbar^2 / 2m(2a - r)^2, & a < r < 2a, \end{cases}$$

$$(14)$$

symmetric around $r = a$ The odd-parity solution of this problem [in the interval $0 < r < a$ corresponding to the radial Schrödinger equation (25) in Sec. IV] fulfills the same boundary condition at $r = a$ as our original model problem. Hence, the Dennison–Uhlenbeck quantization condition (3) with the lower sign chosen and with $V(x)$ changed into $V^{\text{eff}}(r)$, etc. should give the energy levels E_n^a for the compressed atom:

$$2 \int_{r_1}^{r_2} \left(2m[E_n^a - V(r)] - \frac{(l + \tfrac{1}{2})^2 \hbar^2}{r^2} \right)^{1/2} dr$$

$$- 2\hbar \arctan(\tfrac{1}{2} e^{-2K(a)})$$

$$= (k + \tfrac{1}{2}) 2\pi\hbar, \quad k = 0,1,2,\ldots, \qquad (15)$$

where in accordance with (4) and (14)

$$K(a) = \int_{r_2}^{a} \left(\frac{2m}{\hbar^2} [V(r) - E_n] + \frac{(l + \tfrac{1}{2})^2}{r^2} \right)^{1/2} dr, \quad (16)$$

and where

$$\lim_{a \to \infty} E_n^a = E_n, \quad n = k + l + 1. \qquad (17)$$

Substracting (15) from (8), we obtain the following formula for the pressure shift $E_n^a - E_n$:

$$\int_{r_1}^{r_2} \left(\frac{2m}{\hbar^2} [E_n^a - V(r)] - \frac{(l + \tfrac{1}{2})^2}{r^2} \right)^{1/2} dr$$

$$- \int_{r_1}^{r_2} \left(\frac{2m}{\hbar^2} [E_n - V(r)] - \frac{(l + \tfrac{1}{2})^2}{r^2} \right)^{1/2} dr$$

$$= \arctan(\tfrac{1}{2} e^{-2K(a)}), \qquad (18)$$

where r_1 and r_2 are the zeros of the respective integrands on the left of (18).

The approximate formula (18) for the pressure shift $E_n^a - E_n$ of a compressed atom is in complete agreement with first-order results obtained by Fröman, Fröman, and Yngve[5] by means of the method developed by the two former[4] for the rigorous solution of the connection problem. It is however beyond the scope of the present paper to recapitulate the rigorous derivation of formula (18) made in Ref. 5.

Consider now the "compressed hydrogen atom," i.e., let $V(r)$ be given according to (10). Introducing the dimensionless parameter n_a through the relation $E_n^a = -\hbar^2 / (2ma_0^2 n_a^2)$, where according to (13) $n_a \to n$ as $a \to \infty$. Using (10), (18), (16), and (11), we obtain, after some calculations,

$$n_a - n = (1/\pi) \arctan(\tfrac{1}{2} e^{-2K(a)}), \qquad (19)$$

where

$$e^{-2K(a)} = \left(\frac{a/a_0 - n^2 + nQ_a}{a/a_0 - n^2 - nQ_a} \right)^n$$

$$\times \left(\frac{a/a_0 - (l + \tfrac{1}{2})^2 - (l + \tfrac{1}{2})Q_a}{a/a_0 - (l + \tfrac{1}{2})^2 + (l + \tfrac{1}{2})Q_a} \right)^{l + 1/2} e^{-2Q_a},$$

$$(20)$$

and where

$$Q_a = [a^2/(a_0^2 n^2) - 2a/a_0 + (l + \tfrac{1}{2})^2]^{1/2}. \qquad (21)$$

Since

$$-\frac{1}{n_a^2} + \frac{1}{n^2} = (n_a - n) \frac{n_a + n}{n_a^2 n^2} \approx \frac{2(n_a - n)}{n^3} \qquad (22)$$

and

$$\arctan(\tfrac{1}{2} e^{-2K(a)}) \approx \tfrac{1}{2} e^{-2K(a)}, \qquad (23)$$

we obtain the final formula for the energy shift of the compressed hydrogen atom:

$$E_n^a - E_n$$

$$= \frac{1}{2\pi} \frac{\hbar^2}{ma_0^2 n^3} \left(\frac{a/a_0 - n^2 + nQ_a}{a/a_0 - n^2 - nQ_a} \right)^n$$

$$\times \left(\frac{a/a_0 - (l + \tfrac{1}{2})^2 - (l + \tfrac{1}{2})Q_a}{a/a_0 - (l + \tfrac{1}{2})^2 + (l + \tfrac{1}{2})Q_a} \right)^{l + 1/2} e^{-2Q_a}, \quad (24)$$

where Q_a is given by (21).

IV. THE THEORETICAL LAB "COMPRESSED HYDROGEN ATOM"

We still consider an electron in a central potential $V(r)$. In the quantum mechanical treatment of the problem considered in the previous section, we solve the radial Schrödinger equation

$$\frac{d^2 u(r)}{dr^2} + \left(\frac{2m}{\hbar^2} [E - V(r)] - \frac{l(l + 1)}{r^2} \right) u(r) = 0,$$

$$(25)$$

where $u(r)$ is the radial wavefunction. The natural boundary condition

$$u(0) = 0 \qquad (26)$$

selects the regular wavefunction, and this solution of (25) is uniquely determined as for an arbitrary constant factor
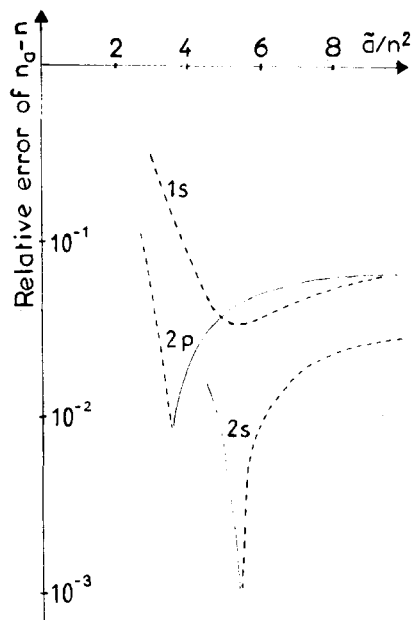
Fig. 3. The relative error of $n_a - n$, i.e., $[(n_a - n)_{approx} - (n_a - n)_{exact}]/(n_a - n)_{exact} = [(n_a)_{approx} - (n_a)_{exact}]/(n_a - n)_{exact}$, is plotted, against $\tilde{a}/n^2 = a/(a_0 n^2)$ for the states $1s$ $(n = 1, l = 0)$, $2s$ $(n = 2, l = 0)$, and $2p$ $(n = 2, l = 1)$. Full drawn lines correspond to a positive error and broken lines to a negative error. It should be mentioned that the cusps in the figure actually correspond to a relative error equal to zero, although for practical reasons this is not seen in the figure.

different from zero. For a bound electron in a free atom we impose the further boundary condition that the wavefunction shall go to zero as $r \to \infty$. The boundary condition for the free atom that $u(r)$ vanishes at infinity is for the model of the compressed atom presented in the previous section replaced by the boundary condition

$$u(a) = 0. \tag{27}$$

When the boundary condition (27) is imposed on the regular solution of (25), we obtain the energy eigenvalues

$$E = E_n^a, \quad n = k + l + 1. \tag{28}$$

Let us now particularize to the case of a compressed hydrogen atom. Introducing into (25) with (10) the substitution (28) with $E_n^a = -\hbar^2/(2ma_0^2 n_a^2)$ and a dimensionless variable and a parameter

$$R = r/a_0, \quad \tilde{a} = a/a_0, \tag{29}$$

we obtain

$$\frac{d^2u}{dR^2} + \left(-\frac{1}{n_a^2} + \frac{2}{R} - \frac{l(l+1)}{R^2} \right) u = 0, \tag{30}$$

with boundary conditions

$$u(R = 0) = u(R = \tilde{a}) = 0. \tag{31}$$

For a numerical calculation of the eigenvalues we approximate the second derivative in the left-hand member of (30) by the second-order difference approximation

$$(u_{\nu+1} - 2u_\nu + u_{\nu-1})/H^2,$$

$$\nu = 1, \ldots, N-1, \quad u_0 = u_N = 0,$$

where

$$H = \tilde{a}/N.$$

The eigenvalue problem (30) with (31) is then reduced to the eigenvalue problem of a symmetric, positively definite tridiagonal matrix of rank $N - 1$. The numerical result for $n_a - n$ is compared with a calculation using formula (19) with (20) and (21). The programming of Eq. (19) on a pocket calculator is left to the students, whereas a numerical program for solving the Schrödinger equation (30) with boundary conditions (31) with the difference approximation method indicated above is available on a VAX computer at our university.

The students are also asked to related the parameter $\tilde{a} = a/a_0$ to the pressure P by assuming that the force F for compressing an atom in the state (n,l) into a sphere of radius a is $-dE_n^a/da$, and the pressure is $F/(4\pi a^2)$.

The accuracy of formula (19) is illustrated in Fig. 3. Considering the crudeness of the model of compression, the accuracy is quite good.

ACKNOWLEDGMENTS

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