Characteristic Values of the Two Minima Problem and Quantum Defects of f States of Heavy Atoms

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The characteristic value problem with two unequal minima in the potential field has been solved by the approximate method of Wentzel, Kramers and Brillouin. The result is applied to the calculation of the quantum defects of the f states of heavy atoms and explains the fact that these quantum defects are all very close to unity

THE quantum mechanical problem in which the potential field possesses two symmetrical minima has been treated by various authors[1] and the results successfully applied to the doubling of energy levels of the ammonia molecule.[2] But the case in which the two valleys in the potential field are not alike has not yet been treated in the literature. This is apparently due to lack of application to physical problems. In the present paper the expression for the eigenvalues of a wave equation with two unsymmetrical potential minima is obtained with the W-K-B method. It is shown that the result finds application in the calculation of certain atomic energy states and, in particular, in the explanation of the fact that the quantum defects of the f states of heavy atoms are all near unity.

I.

Consider the one-dimensional wave equation of a particle of total energy E with a potential function which has two minima. On writing $2mE - 2mV = P^2$, the wave equation takes the form

$$d^2\psi/dx^2 + (4\pi^2/h^2)P^2\psi = 0.$$

The solution of this equation is, in the first approximation,

$$\psi = c_1 P^{-\frac{1}{2}} \exp\ (2\pi i/h) \int^x Pdx$$
$$+ c_2 P^{-\frac{1}{2}} \exp\ (-2\pi i/h) \int^x Pdx.$$

Consider a characteristic value E (Fig. 1) such that in the region I where $x_1 > x$, $P^2 < 0$; in the region II where $x_1 < x < x_2$, $P^2 > 0$; in the region III where $x_2 < x < x_3$, $P^2 < 0$; in the region IV

FIG. 1.

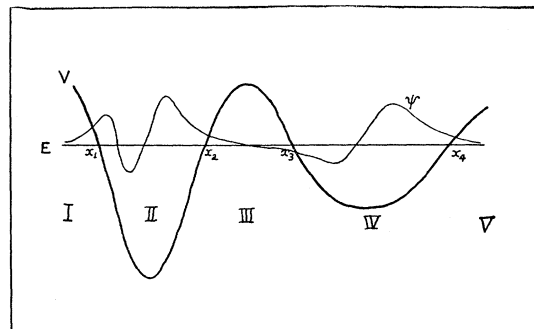where $x_3 < x < x_4$, $P^2 > 0$; and in the region $x_4 < x$, $P^2 < 0$. In the regions II and IV where $P^2 > 0$ and motion is possible classically, ψ has an oscillatory character. In the regions I and V where motion is impossible classically, ψ falls off exponentially; in region III a linear combination of two exponentials must be used.

The relations between the exponential and the oscillatory functions are given by the "connection formulae" of Kramers and Zwaan,[3] obtained

[1] P. M. Morse and E. C. G. Stueckelberg, Helv. Phys. Acta **4**, 337 (1931); P. M. Morse and N. Rosen, Phys. Rev. **40**, 1039A (1932); D. M. Dennison and G. E. Uhlenbeck, Phys. Rev. **41**, 313 (1932).
[2] D. M. Dennison and G. E. Uhlenbeck, reference 1; D. M. Dennison and J. D. Hardy, Phys. Rev. **41**, 313 (1932).

[3] H. A. Kramers, Zeits. f. Physik **39**, 828 (1926); Zwaan, Utrecht Dissertation 1929; L. A. Young and G. E. Uhlenbeck, Phys. Rev. **36**, 1154 (1930).

from considerations of the behavior of the functions in the complex x-plane. The result may be summarized as follows: At a point x_0 where the exponentially increasing or the exponentially decreasing function is to be connected with the oscillatory function, the following formulae hold

$$P^{-\frac{1}{2}} \exp \frac{2\pi}{h} \int_{x_0}^{x} P dx \rightarrow P^{-\frac{1}{2}} \cos\left[\frac{2\pi}{h}\int_{x}^{x_0} P dx + \frac{\pi}{4}\right],\tag{1}$$

$$P^{-\frac{1}{2}} \exp \frac{-2\pi}{h} \int_{x_0}^{x} P dx \rightarrow 2P^{-\frac{1}{2}} \cos\left[\frac{2\pi}{h}\int_{x}^{x_0} P dx - \frac{\pi}{4}\right].$$

Here, and in all that follows, P is taken to mean $(|2mE - 2mV|)^{\frac{1}{2}}$.

Now at x_1, the exponentially decreasing function in the region $x < x_1$

$$\psi_{\mathrm{I}} = AP^{-\frac{1}{2}} \exp\left(-2\pi/h\right) \int_{x}^{x_1} P dx$$

is connected with the oscillatory function to the right of x_1

$$\psi_{\mathrm{II}_a} = 2AP^{-\frac{1}{2}} \cos\left[\left(2\pi/h\right) \int_{x_1}^{x} P dx - \pi/4\right].$$

At the right of x_2, we have a linear combination of increasing and decreasing exponentials

$$\psi_{\mathrm{III}_a} = DP^{-\frac{1}{2}} \exp\left(2\pi/h\right) \int_{x_2}^{x} P dx$$

$$+ EP^{-\frac{1}{2}} \exp\left(-2\pi/h\right) \int_{x_2}^{x} P dx.$$

By (1) the continuation of this into region II is

$$\psi_{\mathrm{II}_b} = P^{-\frac{1}{2}} \cos\left[\left(2\pi/h\right) \int_{x}^{x_2} P dx - \pi/4 + \delta\right],$$

where

$$\tan \delta = D/2E.\tag{2}$$

As ψ_{II_a} and ψ_{II_b} are the same function, they, together with their derivatives, must be equal and hence

$$(d\psi_{\mathrm{II}_a}/dx)/\psi_{\mathrm{II}_a} = (d\psi_{\mathrm{II}_b}/dx)/\psi_{\mathrm{II}_b}.$$

From this it follows that

$$(2\pi/h) \int_{x_1}^{x_2} P dx = (n+1/2)\pi - \delta.\tag{3}$$

At x_4, the decreasing function

$$\psi_{\mathrm{V}} = BP^{-\frac{1}{2}} \exp\left(-2\pi/h\right) \int_{x_4}^{x} P dx$$

is connected with the oscillatory function to the left of x_4

$$\psi_{\mathrm{IV}_a} = 2BP^{-\frac{1}{2}} \cos\left[\left(2\pi/h\right) \int_{x}^{x_4} P dx - \pi/4\right].$$

To extend the solution ψ_{III_a} into region IV, it may be noted that ψ_{III_a} may be written in the form

$$\psi_{\mathrm{III}_b} = D\alpha^2 P^{-\frac{1}{2}} \exp\left(-2\pi/h\right) \int_{x}^{x_3} P dx$$

$$+ E\alpha^{-2} P^{-\frac{1}{2}} \exp\left(2\pi/h\right) \int_{x}^{x_3} P dx,\tag{4}$$

where

$$\alpha^2 = \exp\left(2\pi/h\right) \int_{x_2}^{x_3} P dx.$$

By (1) the continuation of ψ_{III_b} into region IV is

$$\psi_{\mathrm{IV}_b} = P^{-\frac{1}{2}} \cos\left[\left(2\pi/h\right) \int_{x_3}^{x} P dx - \pi/4 + \epsilon\right],$$

where

$$\tan \epsilon = E/2D\alpha^4.\tag{5}$$

As ψ_{IV_a} and ψ_{IV_b} are the same function, we have as before

$$(2\pi/h) \int_{x_3}^{x_4} P dx = (n+1/2)\pi - \epsilon.\tag{6}$$

From (2) and (5) we obtain the relation between δ and ϵ

$$\tan \delta \tan \epsilon = 1/4\alpha^4.\tag{7}$$

The characteristic value E is then given by (3), (6) and (7) which, on combining, may be written in the form

$$(2\pi/h) \int_{x_1}^{x_2} P dx = (n+1/2)\pi - \arctan\left[(1/4)\exp\left\{(-4\pi/h)\int_{x_2}^{x_3} P dx\right\} \cdot \tan\left(2\pi/h\right)\int_{x_3}^{x_4} P dx\right].\tag{8}$$

An immediate result of this equation is that when the two minima of the potential field are exactly symmetrical,

$$\delta = \epsilon, \quad \text{and} \quad \delta = \pm\tan^{-1}(1/2\alpha^2).$$

This shows that to a first approximation, each energy level is split in two symmetrically with respect to the one that would exist if there is only one valley in the field. Furthermore, this splitting, which results from the resonance between the two energy states in the two potential valleys, increases as the square root area under the potential hill decreases. This agrees with the results of Dennison and Uhlenbeck[1] on the doubling of the vibrational levels of the ammonia molecule.

II.

The above result finds application in the calculation of certain atomic energy levels. In a central field the wave equation satisfied by the radial wave function ψ/ρ is

$$d^2\psi/d\rho^2 + (E - V)\psi = 0 \quad \text{with} \quad V = v + l(l+1)/\rho^2, \tag{9}$$

the energy E and the potential energy v being in units of the ionization potential of hydrogen and the atomic distance ρ in units of the first Bohr radius of hydrogen. With the aid of an atomic field, such as that of Fermi-Thomas, the energies can be obtained by solving Eq. (9) with the W-K-B method.

To calculate the energy values in the arc spectrum, one may consider the electron as moving in the field of the singly ionized atom and for v one may use the Fermi potential[4] for a singly charged positive ion. Thus

$$v = -(2Z/\rho)\varphi(\gamma\rho) - 2/\rho_0, \quad \rho < \rho_0; \quad v = -2/\rho, \quad \rho > \rho_0$$

where $\gamma = (128\,Z/9\pi^2)^{\frac{1}{3}}$, ρ_0 is the distance beyond which the field is of Coulombian character, i.e., $\varphi(\gamma\rho_0) = 0$, and φ is the Fermi function for a singly ionized atom of nuclear charge Z. Thus φ satisfies the equations

$$d^2\varphi/dx^2 = \varphi^{\frac{3}{2}}/x^{\frac{1}{2}}, \quad x < x_0; \quad d^2\varphi/dx^2 = 0, \quad x > x_0$$

subject to the conditions $\varphi(0) = 1$, $-x_0(d\varphi/dx)_{x_0} = 1/Z$, where $x = \gamma\rho$.

Solution of Eq. (9) by the W-K-B method leads to the phase integral of the classical quantum theory with half integer quantization in all cases in which V possesses one minimum. But in certain cases, such as the d states of the elements of the third and the fourth periods and the f states of the heavy atoms, the V function has two valleys separated by a potential hill. The curves of V for the f states of Hg, U, U$^+$, U^{++} and U^{+++} are given in Fig. 2. The inner valley is a very deep and narrow one; in the case of uranium its minimum lies at -79.5 and can not be conveniently shown in the figure.

From the curves of V it is evident that the energies of the f states of heavy neutral atoms must be calculated by means of Eq. (8) which, after a transformation to the atomic units is made, takes the form[5]

$$\int_{\rho_3}^{\rho_4} Q d\rho = (n - l - 1/2)\pi - \arctan\left[(1/4)\left\{\exp\left(-2\int_{\rho_2}^{\rho_3} Q d\rho\right)\right\}\tan\int_{\rho_1}^{\rho_2} Q d\rho\right], \tag{8a}$$

where

$$Q = \{|E - v - (l+1/2)^2\rho^{-2}|\}^{-\frac{1}{2}}.$$

Here $\int_{\rho_1}^{\rho_2} Q d\rho$, $\int_{\rho_3}^{\rho_4} Q\,d\rho$ are the phase integrals taken over the inner and the outer regions of possible classical motion, respectively, and $\int_{\rho_2}^{\rho_3} Q\,d\rho$ is taken over the potential barrier between them. In the calculation of E for the f states, a great simplicity sets in, as the field in the region $\rho_3 < \rho < \rho_4$ is of

[4] E. Fermi, *Mem. della reale Acad. d'Italia* I (1930); A. Sommerfeld, Zeits. f. Physik **78**, 283 (1932).

[5] The result of Sugiura and Urey, Kgl. Danske Vid. Selsk. **7**, 13 (1926), concerning the energy levels of the f states of elements of the 6th and the 7th periods must be modified by replacing the Sommerfeld phase integral by Eq. (8) above. See T. Y. Wu and S. Goudsmit, Phys. Rev. **43**, 496 (1933).
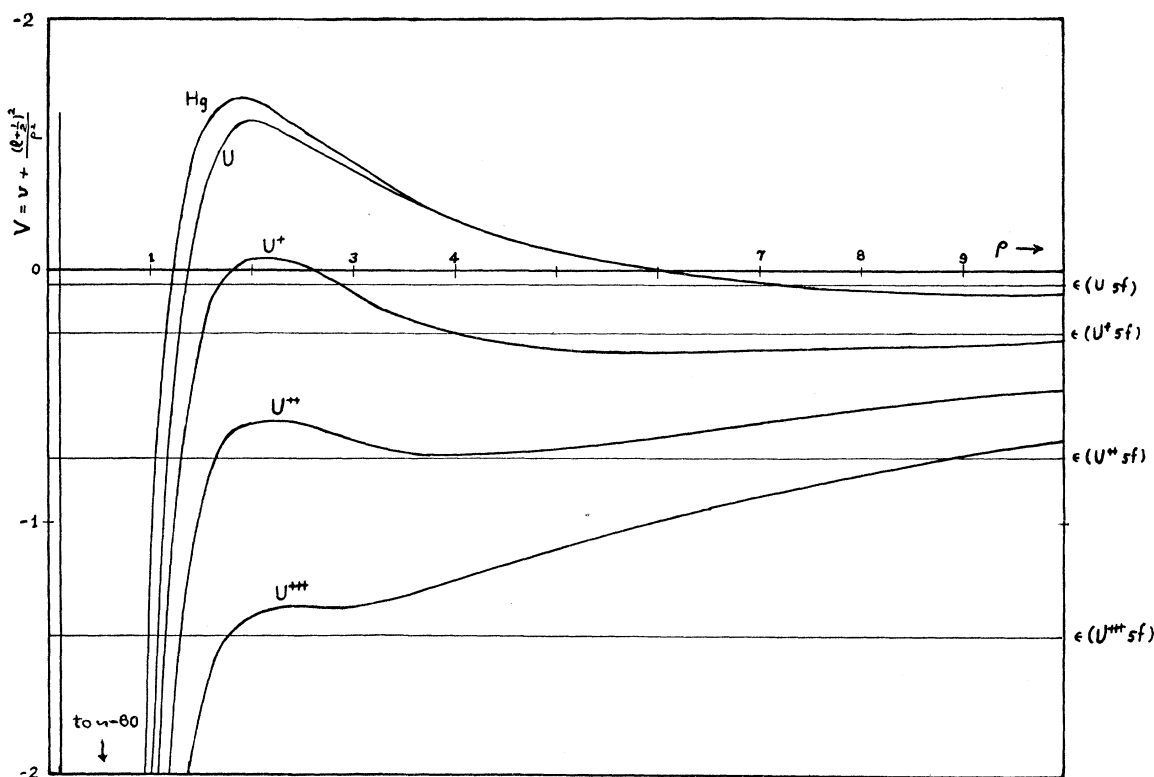
FIG. 2. Curves of $V = v + (l + \frac{1}{2})^2 \rho^{-2}$ for f states of heavy atoms and ions.

Coulombian nature. The integral $\int_{\rho_3}^{\rho_4} Q d\rho$ can be evaluated directly giving

$$\int_{\rho_3}^{\rho_4} [E - 2/\rho - (l + 1/2)^2 \rho^{-2}]^{\frac{1}{2}} d\rho = \pi(-E)^{-\frac{1}{2}} - \pi(l + 1/2). \tag{10}$$

Writing

$$\arctan\left[(1/4)\left\{\exp\left(-2\int_{\rho_2}^{\rho_3} Q d\rho\right)\right\} \tan \int_{\rho_1}^{\rho_2} Q d\rho\right] = \Delta\pi, \tag{11}$$

we have, on combining Eqs. (8a) and (10)

$$E = -1/(n - \Delta)^2. \tag{12}$$

It can be easily shown that when one's attention is confined to the discrete states, Δ is a very slowly varying function of E. Hence the above expression may be regarded as a Rydberg formula with a quantum defect Δ.

The values E are found by so adjusting them that Eq. (8a) is satisfied. Then Δ is calculated according to Eq. (11). The calculations can be carried out with the aid of a planimeter. It is found that for all neutral atoms from Au $(Z = 79)$ to U $(Z = 92)$, the integral $\int_{\rho_1}^{\rho_2} Q d\rho$ over the inner classical region varies from 1.0π to 1.2π and the potential hill is so large that the factor $\exp(-2 \int_{\rho_2}^{\rho_3} Q d\rho)$ ranges from 0.0027 to 0.0025. A little consideration will hence show that $\Delta = 1.00$ for the f states of all these atoms. The experimental values of Δ of these states are listed in Table I.[6] The difference between the observed values and the expected values 1.00 of the quantum defects may be attributed

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[6] The closeness of the effective quantum numbers of these states to 4 has led many authors to assign the value 4 to the principal quantum numbers. See, for example, Hund's *Linienspektren und periodisches System der Elemente*, p. 42.

to the effect of polarization of the atomic core, which has been neglected, and the approximate nature of the calculation.

TABLE I. *Experimental values of* Δ.

Z	79	80	81	82	86
Atom	Au	Hg	Tl	Pb	Rn
Δ	1.03	1.03	1.02	1.04	1.02

SOME REMARKS ON THE CALCULATION OF ENERGY LEVELS WITH THE FERMI POTENTIAL FOR POSITIVE IONS

Calculations of the energy levels of the heaviest atoms and ions have been made[5] with the Fermi potential for positive ions. Further calculations show that the calculated levels invariably lie above the observed positions by amounts which are different for the s, p, d, f states and which are quite large in the case of atoms of medium atomic weights but become smaller for the heavy atoms, as shown by Table II.

TABLE II.

	$6s$ Cs	$7s$ Tl	$6p$ Cs	$7s$ Ra$^+$	$7p$ Ra$^+$	$6d$ Ra$^+$	$5d$ Ce^{+++}	$4f$ Ce^{+++}
Calc. E	−0.215	−0.188	−0.145	−0.54	−0.47	−0.55	−1.65	−1.08
Obs. E	−0.286	−0.209	−0.184	−0.795	−0.56	−0.665[7]	−1.90	
Difference	0.071	0.021	0.039	0.255	0.09	0.115	0.25	

The energies here are expressed in terms of the Rydberg constant. It is seen that energy levels obtained with the statistical potential are at best qualitative. In spite of the consistent discrepancy between the calculated and the observed values, the relative positions of the $5d$ and the $4f$ levels of Ce^{+++} seem to be correct; for it does not seem very likely that the correction for the calculated $4f$ level is so large as to reverse them. This is of some interest, for on the other hand, the data on the magnetic susceptibilities of tri-valent cerium salts, hydrated or in solution, apparently show that the lowest states of Ce^{+++} are $4f\,^2F$. Spectroscopically the $4f$ levels have not yet been found[8] and these rough calculations indicate that they are approximately 60,000 cm^{-1} above the $5d$ levels. Further analysis of the spectrum of Ce^{+++} is desirable.

Calculations of doublet separations and values of $\psi^2(0)$ for s electrons have been made with the Fermi potential for positive ions. The characteristic functions needed are obtained by solving the wave equation by the W-K-B method. The results are in better agreement with observed values or with Breit's more accurate calculations than are those obtained with the use of the Thomas-Fermi potential for neutral atoms, as shown by the Table III.

TABLE III.

	Calc. with potential for positive ions	Obs.	Calc. with potential for neutral atoms
$\Delta\nu(6p\,^2P_{\frac{3}{2}} - 6p\,^2P_{\frac{1}{2}})$ Cs	400 cm^{-1}	554 cm^{-1} Breit[11]	1022 cm^{-1} [9]
$\psi^2(0)$ for $6s\,^2S_{\frac{1}{2}}$ Cs	1.51×10^{26}	1.8×10^{26}	2.7×10^{25} [10]
$\psi^2(0)$ for $7s\,^2S_{\frac{1}{2}}$ Tl	1.88×10^{25}	1.7×10^{25}	

The writer is very grateful to Professor S. Goudsmit for his advice and interest in this problem.

[7] W. Albertson, Phys. Rev. 39, 385 (1932).

[8] Freed, also Serber, have attributed the absorption at 2400Å of cerium salts to the transition $4\,^2F \rightarrow 5\,^2D$, taking $4\,^2F$ as the normal state. Cf. C. J. Gorter, Phys. Zeits. 34, 238 (1933).

[9] G. Gentile and E. Majorana, Accad. Lincei. Atti 8, 229 (1928).

[10] E. Fermi, Zeits. f. Physik 60, 320 (1930).

[11] G. Breit, Phys. Rev. 42, 348 (1932).