

Derivation of Sommerfeld-Dirac Fine-Structure Formula by WKB Method

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Using the WKB approximation in the spirit of Miller and Good, we have obtained an expression which connects the energy eigenvalues of two parts: One is supposedly known and the other is to be solved. We use the Balmer energy formula of the one-electron bound state as the known part and solve for its relativistic counterpart, the Sommerfeld-Dirac fine-structure formula. An exact form of the relativistic energy-level formula can be obtained through this modified WKB expansion to order \hbar^2 .

1. INTRODUCTION

The problem we are to discuss here is that of finding the relativistic energy eigenvalue formula for the one-electron bound-state problem by means of the modified WKB method in the spirit of Miller and Good.¹ The ordinary WKB method cannot give the right form of the bound-state energy eigenvalue. The right form was given in the paper by Good,² where he discussed the unpublished work of Bassey and Uhlenbeck, and applied their modified WKB approximation to the bound states of the single-electron atom. The result is good only for large quantum numbers. The purpose of this paper is to report some further progress in this direction, namely, if use is made of the eigenvalue relationship derived by the author,³ the correct Sommerfeld-Dirac fine-structure formula is obtained. In this derivation, we consider the Balmer formula or the nonrelativistic part of the problem to be already known while we solve for its relativistic part. The general formula used is more restricted but more manageable than that given by Rosen and Yennie.⁴ However, the result obtained is surprisingly good, as we can derive the exact form of the relativistic Sommerfeld-Dirac energy formula by this modified WKB expansion to order \hbar^2 .

2. DERIVATION OF SOMMERFELD-DIRAC FINE-STRUCTURE FORMULA

We use Eq. (4) of Ref. 3 with some modifications. One of that equation's characteristics is that the variables of the known part and the unknown part are separable. Starting with the Dirac radial wave equations, we have

$$V(r) = -Z|e^2|/r,$$

$$\frac{W - V(r) + mc^2}{\hbar c} u - \frac{d}{dr} v + \frac{l+1}{r} v = 0, \quad (1)$$

$$\frac{W - V(r) - mc^2}{\hbar c} v + \frac{d}{dr} u + \frac{l+1}{r} u = 0.$$

From Eqs. (1), we get

$$\frac{d^2}{dr^2} M(r) - F(r) \frac{dM(r)}{dr} + \left(\frac{mc}{\hbar} F(r) + \frac{f(r)g(r)}{\hbar^2} - \frac{m^2 c^2}{\hbar^2} \right) M(r) = 0, \quad (2)$$

$$\text{with } M = u + v, \quad f = \frac{1}{c} \left(W + \frac{Z|e^2|}{r} \right) - \left(\frac{l+1}{r} \right) \hbar,$$

$$g = \frac{1}{c} \left(W + \frac{Z|e^2|}{r} \right) + \left(\frac{l+1}{r} \right) \hbar, \quad \text{and } \frac{1}{f} \frac{df}{dr} = F.$$

We proceed on the basis of the solved problem of the differential equation

$$\frac{d^2}{ds^2} M_0(s) + \frac{P^2(2)}{\hbar^2} M_0(s) = 0, \quad (3)$$

by setting $M(r) = a(r)M_0(s(r))$, with $a(r)$ and $s(r)$ the relationships to be determined. We get, after some algebraic details, essentially in the same way as in Eq. (4) in Ref. 3,

$$\oint \left\{ [fg - (mc)^2]^{1/2} + \frac{1}{2} mc \hbar \frac{F}{[fg - (mc)^2]^{1/2}} + \hbar^2 \frac{2F' - F^2}{8[fg - (mc)^2]^{1/2}} - \hbar^2 \frac{1}{8} (mc)^2 \frac{F^2}{[fg - (mc)^2]^{3/2}} + \hbar^2 \frac{1}{8[fg - (mc)^2]^{1/2}} \right.$$

$$\times \left[3 \left(\frac{(d/dr)[fg - (mc)^2]^{1/2}}{[fg - (mc)^2]^{1/2}} \right)^2 - \frac{2(d^2/dr^2)[fg - (mc)^2]^{1/2}}{[fg - (mc)^2]^{1/2}} \right] dr = \oint \left[P - \frac{1}{8}\hbar^2 \left(\frac{2P''}{P^2} - \frac{3P'^2}{P^3} \right) \right] ds. \quad (4)$$

The contour integrals are evaluated by going around the turning points of the problem. We let the supposedly known part [Eq. (3)] be the Schrödinger equation of the single-electron bound-state problem with

$$P^2(s) = 2m \left(E_H + \frac{Z|e^2|}{s} \right) - L \frac{(L+1)\hbar^2}{s^2},$$

and E_H (the Balmer energy formula)

$$= -\frac{mZ^2|e^2|^2}{2(n+L+1)^2\hbar^2}, \quad n=0, 1, 2, \dots$$

Note here that the angular momentum quantum number L is different than the l used before. The integrals in the right-hand side of Eq. (4) have already been evaluated.⁵ If we include the terms of higher orders in \hbar^2 , we get the sum $2\pi\hbar(n + \frac{1}{2})$, with $n=0, 1, 2, \dots$ for the whole thing. In the processes of evaluation, use is made of the external differentiation given by Krieger *et al.*⁶ Actually, this method gives the same results as the ordinary method of integration by parts. This interchangeability of the external-differentiation method used by Krieger *et al.* in evaluating the contour integrations with the method of integration by parts facilitates the integrations in the left-hand side, too.

Thus, Eq. (4) reduces to

$$\oint \left\{ [fg - (mc)^2]^{1/2} + \hbar \frac{1}{2} mc \frac{F}{[fg - (mc)^2]^{1/2}} + \hbar^2 \frac{2F' - F^2}{8[fg - (mc)^2]^{1/2}} - \hbar^2 \frac{1}{8} (mc)^2 \frac{F^2}{[fg - (mc)^2]^{3/2}} + \hbar^2 \frac{1}{8[fg - (mc)^2]^{1/2}} \right. \\ \left. \times \left[3 \left(\frac{(d/dr)[fg - (mc)^2]^{1/2}}{[fg - (mc)^2]^{1/2}} \right)^2 - \frac{2(d^2/dr^2)[fg - (mc)^2]^{1/2}}{[fg - (mc)^2]^{1/2}} \right] \right\} dr = 2\pi\hbar(n + \frac{1}{2}), \quad n=0, 1, 2, \dots, \quad (5)$$

which is identical with Bassey's equation [Eq. (14) in Ref. 2] except for the higher-order terms. Listed below are the important formulas that are used (consider $a < 0$):

$$\oint \frac{dx}{x(a+bx+cx^2)^{1/2}} = \frac{2\pi}{(-a)^{1/2}},$$

$$\oint \frac{dx}{x^2(a+bx+cx^2)^{1/2}} = \frac{b\pi}{(-a)^{3/2}},$$

$$\oint \frac{dx}{x(a+bx+cx^2)^{3/2}} = \frac{1}{2} \oint \frac{dx}{x(a+bx+cx^2)^{1/2}} = \frac{-2\pi}{(-a)^{3/2}},$$

$$\text{and } \oint \frac{dx}{x^2(a+bx+cx^2)^{3/2}} \\ = -\frac{3b}{2a} \oint \frac{dx}{x(a+bx+cx^2)^{3/2}} = \frac{-3b\pi}{(-a)^{5/2}}.$$

By means of these formulas, it is possible to evaluate the following integrals:

$$\oint [fg - (mc)^2]^{1/2} dr = \frac{WZ|e^2|}{c^2} \frac{2\pi}{[(mc)^2 - (W/c)^2]^{1/2}}$$

$$- 2\pi \left[(l+1)^2 \hbar^2 - \left(\frac{Z|e^2|}{c} \right)^2 \right]^{1/2},$$

$$\oint \frac{F}{[fg - (mc)^2]^{1/2}} dr = \frac{2\pi}{mc},$$

$$\oint \frac{2F' - F^2}{[fg - (mc)^2]^{1/2}} dr = \frac{4\pi W}{mc^2[(l+1)\hbar - Z|e^2|/c]}$$

$$- \frac{6\pi(l+1)\hbar W^3}{(mc^2)^3[(l+1)\hbar - Z|e^2|/c]^2} + \frac{2\pi}{[(l+1)^2\hbar^2 - (Z|e^2|/c)]^{1/2}},$$

$$\oint \frac{1}{[fg - (mc)^2]^{1/2}} \left[3 \left(\frac{d/dr[fg - (mc)^2]^{1/2}}{[fg - (mc)^2]^{1/2}} \right)^2 \right.$$

$$\left. - 2 \frac{d^2/dr^2[fg - (mc)^2]^{1/2}}{[fg - (mc)^2]^{1/2}} \right] dr$$

$$= -\frac{2\pi}{\hbar[(l+1)^2 - (Z|e^2|/\hbar c)^2]^{1/2}}$$

$$\text{and } \phi \frac{F^2}{[fg - (mc)^2]^{3/2}} = \frac{4\pi W}{m^3 c^4} \frac{1}{[(l+1)\hbar - Z|e^2|/c]} \times \left[(l+1)^2 \hbar^2 - \left(\frac{Z|e^2|}{c} \right)^2 \right]^{1/2} = 2\pi \hbar (n + \frac{1}{2}). \quad (6)$$

Solving for W

$$-\frac{6\pi W^3}{m^3 c^8} \frac{(l+1)\hbar}{[(l+1)\hbar - Z|e^2|/c]^2} \quad W = mc^2 \left\{ 1 + \left(\frac{Z|e^2|}{\hbar c} \right)^2 \right\} / \left[n + (l+1)^2 - \left(\frac{Z|e^2|}{\hbar c} \right)^2 \right]^{1/2} \quad (7)$$

We get, therefore, by substitution of the above into Eq. (5) and after some cancellations,

$$\frac{2\pi W Z |e^2|}{c^2 [(mc)^2 - (W/c)^2]^{1/2}} + \hbar \pi - 2\pi$$

Here, we recall that $n = 0, 1, 2, \dots$ and $l \neq -1$. This is the Sommerfeld-Dirac fine-structure formula.

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Virtual Orbitals in Hartree-Fock Theory*

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An arbitrariness of virtual orbitals in the Hartree-Fock theory is discussed, and it is explicitly demonstrated that the energy spectrum of the virtual orbitals can be manipulated so that the convergence property may be improved in the perturbation theory and the configuration interaction calculation based on the Hartree-Fock equation.

INTRODUCTION

In the Hartree-Fock theory of many-electron systems, the occupied orbitals are the only orbitals physically relevant; but since we usually obtain the occupied orbitals from some kind of eigenvalue equations which give us more orbitals than needed to accommodate the electrons of the system, we have the so-called virtual orbitals. In many cases, they have no use and accordingly they are simply ignored.

There are certain cases, however, in which we do need to use those virtual orbitals resulting from the Hartree-Fock eigenvalue equation. Among them are the configuration interaction calculation and the perturbation calculation based on the Hartree-Fock solutions. As an example we shall discuss Kelly's many-body perturbation theory applied to Be.^{1,2}

For a closed-shell electron configuration of atoms and molecules, the Hartree-Fock operator F may be written (in a. u.)

$$F = -\frac{1}{2} \Delta - \sum_a (Z_a/r_a) + \sum_{i, \text{occ}} (2J_i - K_i), \quad (1)$$

and the Hartree-Fock equation is

$$F \phi_i = \epsilon_i \phi_i. \quad (2)$$

Here the suffix i numbers doubly occupied orbitals. The operators J_i and K_i are defined as follows:

$$J_i(\nu)\phi(\nu) = \int \phi_i^*(\mu)\phi_i(\mu) \frac{1}{r_{\mu\nu}} dV_\mu \times \phi(\nu), \quad (3)$$

$$K_i(\nu)\phi(\nu) = \int \phi_i^*(\mu)\phi(\mu) \frac{1}{r_{\mu\nu}} dV_\mu \times \phi_i(\nu). \quad (4)$$

For the $(1s)^2(2s)^2^1S$ state of the Be atom, we have