

CHAPTER III

THE QUANTUM DEFECT METHOD

3.1 Introduction

Recent attempts to determine theoretically the wave functions and the energy levels have demonstrated that the amount of labour involved in such a study is enormous, even if one endeavors to simplify the problem by making some quite restrictive assumptions concerning the form of the many-particle wave function. It was, therefore, of interest when a procedure called the Quantum Defect Method (QDM) was proposed which made short-cuts in the calculations possible. The present form of the QDM is a development of a procedure originated by Kuhn and Van Vleck (1950) and has been significantly refined and extended by Brooks (1953, 1958; Brooks and Ham, 1958) and by Ham (1954, 1955).

3.2 Fundamental Features

The essential idea of the QDM is as follows. In a free atom of an alkali metal, the valence electron is loosely bound to a compact spherical core of electrons in closed shells. The closed shells are not modified when the atoms begin to form into solid. The compact core occupies only a small portion of the volume of an atomic cell. For this reason, the electrostatic field which acts on the valence electron is nearly a pure coulomb field through out most of the cell. Hence its wave function must be a coulomb wave function in the outer region of the cell. The same is true in the free atom. It does not imply, however, that the wave function is

hydrogenic. The solutions of the Schrödinger equation with a coulomb potential are two linearly independent confluent hypergeometric functions. For a given energy, there is a unique "coupling constant" which determines the combination of these two functions which will vanish exponentially at infinity. If it is assumed that the coupling constant depends smoothly on energy, so that it would be possible to extrapolate it as a function of energy, and hence to determine it for any energy. This coupling constant is, in reality, determined by solving the Schrödinger equation with the actual potential energy inside the core. It is possible, however, to determine this constant empirically without taking explicit account of interaction within the core.

To formalize this discussion, we consider the radial wave equation which can be expressed in the atomic unit as

$$\frac{d^2 U_\ell}{dr^2} + \left[-\frac{1}{n^2} + \frac{2}{r} - \frac{\ell(\ell+1)}{r^2} \right] U_\ell = 0 \quad (3.2.1)$$

The potential $V(r) = -\frac{2}{r}$ and the energy E is replaced by $-\frac{1}{n^2}$ (n is an integer only in the hydrogenic problem) since we are concerned with the outer regions of the cell. One of the two linearly independent solutions, $U_{\ell,0}$, vanishes at the origin and the other, $U_{\ell,1}$, is singular there. Consequently, $U_{\ell,1}$ could not appear in the usual hydrogenic problem. The functions may be expressed in terms of Bessel functions (Wannier, 1943; Kuhn, 1951; Ham, 1957)

$$U_{\ell,0}(n,r) = \frac{z}{2} J_{2\ell+1}^n(z) = \frac{n^{\ell+1}}{\Gamma(2\ell+1)} M_{n,\ell+\frac{1}{2}}\left(\frac{2r}{n}\right) \quad (3.2.2)$$

$$U_{l,1}(n,r) = \frac{z}{2} N_{2l+1}^n(z) \quad (3.2.3)$$

in which

$$z = (8r)^{1/2} \quad (3.2.4)$$

The functions J_{2l+1}^n , N_{2l+1}^n are combinations of Bessel functions, $M_{n,l+1/2}$ is a regular Whittaker function and $\Gamma(2l+1)$ is a Gamma function. The general solution of eq.(3.2.1) is now expressed as

$$U_l(r) = \alpha(n) U_{l,0}(n,r) + \gamma(n) U_{l,1}(n,r) \quad (3.2.5)$$

where $\alpha(n)$ and $\gamma(n)$ are coupling constants which depend on only n . Both $U_{l,0}$ and $U_{l,1}$ are present because the potential inside the core region is not coulombic.

The problem is now to determine the ratio $\alpha(n)/\gamma(n)$.

At an eigenvalue of the free atom, the wave function goes to zero exponentially at infinity and, consequently, must be represented by the function $W_{n,l+1/2}(\frac{2r}{n})$ which has this property. This function is called the Whittaker function and is given in relation with the quasi-Bessel functions J_{2l+1}^n , N_{2l+1}^n by Whittaker and Watson (1952) as

$$W_{n,l+1/2}(\frac{2r}{n}) = \frac{\Gamma(n+l+1)}{n^{l+1}} \left(\frac{z}{2}\right) J_{2l+1}^n(z) \cos \pi(n-l-1) + \Gamma(n-l) n^l \left(\frac{z}{2}\right) N_{2l+1}^n(z) \sin \pi(n-l-1) \quad (3.2.6)$$

Hence at an eigenvalue of the free atom the ratio $\alpha(n)/\gamma(n)$ is determined to be :

$$\frac{\alpha(n)}{\gamma(n)} = \frac{\Gamma(n+l+1)}{n^{2l+1} \Gamma(n-l) \tan \pi(n-l-1)} \quad (3.2.7)$$

For any energy, the ratio $\alpha(n)/\delta(n)$ is defined as

$$\frac{\alpha(n)}{\delta(n)} = - \frac{\Gamma'(n+l+1)}{n^{2l+1} \Gamma(n-l) \tan \pi \nu(n)} \quad (3.2.8)$$

When the two previous equations are compared we see that

$$\nu(n) = m' + l + 1 - n \quad (3.2.9)$$

where m' is an arbitrary integer. The energy at an eigenvalue is

$$E = -\frac{1}{n^2} = -\frac{1}{(m-\nu)^2} \quad (3.2.10)$$

in which $m = m' + l + 1$ is an integer. Consequently, ν differs from the experimental quantum defect μ by an integer at most. The fundamental procedure of the QDM is to set $\nu = \mu$ at energies corresponding to the eigenvalues of the free atom. Since $\nu = \mu$ occurs when $m' = 0$, the integer m is then equal to $l+1$ which is the principal quantum number \mathcal{N} . We can rewrite eq.(3.2.10) as

$$E = -E = \frac{1}{(n-\mu)^2} \text{ Rydberg} \quad (3.2.11)$$

μ is known as the quantum defect.

3.3 Relation of the Quantum Defect to the Effective Potential

It was shown in the previous section that the QDM was developed in order to calculate the energy levels of an alkali metal by extrapolation of the quantum defects obtained from the observed energy spectra of the free atom. It is easy to calculate the energy levels of the free atom if the quantum defect is known.

The quantum defect, of course, depends upon the (effective) potential of the core; the relation between these two quantities was recently shown by Jaffé and Reinhardt (1977). The relation is employed to obtain the quantum defect and the energy level is then determined by means of eq.(3.2.11). The constructed potential is finally examine by comparing the reproduced energy levels against the experimental data.

The required relation is derived by starting with the Hamilton-Jacobi equation with the Hamiltonian expressed in the spherical coordinates :

$$H = \frac{1}{2m} \left(p_r^2 + \frac{p_\theta^2}{r^2} + \frac{p_\phi^2}{r^2 \sin^2 \theta} \right) - V(r) \quad (3.3.1)$$

where p_r, p_θ, p_ϕ are the canonical momenta for each coordinate in the spherical coordinates and $V(r)$ is the potential energy which depends on r only.

The Hamilton-Jacobi equation with total energy E can be written as

$$\left\{ \left(\frac{\partial S}{\partial r} \right)_{\theta, \phi}^2 + \frac{1}{r^2} \left[\left(\frac{\partial S}{\partial \theta} \right)_{r, \phi}^2 + \frac{1}{\sin^2 \theta} \left(\frac{\partial S}{\partial \phi} \right)_{r, \theta}^2 \right] \right\} - 2m[E - V(r)] = 0 \quad (3.3.2)$$

where S is the same as the characteristic function W given by Goldstein(1959) in eq.(9-61).

We set the trial solution as

$$S(r, \theta, \phi) = S(r) + S(\theta) + S(\phi). \quad (3.3.3)$$

It has been found that the only dependence on ϕ occurs in the last term when S is substituted into eq.(3.3.2).

Since the equation is to be true for all ϕ , we set



$$\left(\frac{\partial S}{\partial \phi}\right)_{r,\theta} = p_\phi = \beta_\phi \quad (3.3.4)$$

as one of the constant of integration.

The Hamilton-Jacobi equation now reduces to

$$\left[\left(\frac{\partial S}{\partial r}\right)_{\theta,\phi}^2 + \frac{1}{r^2} \left\{ \left(\frac{\partial S}{\partial \theta}\right)_{r,\phi}^2 + \frac{\beta_\phi^2}{\sin^2 \theta} \right\} \right] - 2m[E - V(r)] = 0. \quad (3.3.5)$$

Again, the term in the curly brackets involves θ only and must therefore be equal to another constant :

$$\left(\frac{\partial S}{\partial \theta}\right)_{r,\phi}^2 + \frac{\beta_\phi^2}{\sin^2 \theta} = \beta_\theta^2 \quad (3.3.6)$$

Eq.(3.3.6) can be rewritten as

$$\left(\frac{\partial S}{\partial \theta}\right)_{r,\phi} = p_\theta = \left(\beta_\theta^2 - \frac{\beta_\phi^2}{\sin^2 \theta}\right)^{1/2}. \quad (3.3.7)$$

Similarly, it is found that

$$\left(\frac{\partial S}{\partial r}\right)_{\theta,\phi} = p_r = \left(2m[E - V(r)] - \frac{\beta_\theta^2}{r^2}\right)^{1/2}. \quad (3.3.8)$$

By defining the action integral

$$I_k = \frac{1}{2\pi} \oint_k p_k dq_k, \quad (3.3.9)$$

we have

$$I_\phi = \frac{\beta_\phi}{2\pi} \oint d\phi = \beta_\phi, \quad (3.3.10)$$

$$I_\theta = \frac{1}{2\pi} \oint \left\{ \beta_\theta^2 - \frac{\beta_\phi^2}{\sin^2 \theta} \right\}^{1/2} d\theta = \beta_\theta - \beta_\phi, \quad (3.3.11)$$

and

$$I_r = \frac{1}{2\pi} \oint \left\{ 2m[E - V(r)] - \frac{\beta_\theta^2}{r^2} \right\}^{1/2} dr. \quad (3.3.12)$$

I_r depends on the potential $V(r)$ and is not usually analytically integrable. The integral in eq.(3.3.11) for I_θ is performed by a

procedure suggested by Van Vleck (1926) :

It will be recalled from eq.(2-51) of Goldstein(1959) that when the defining equations for the generalized coordinates do not involve time explicitly then

$$2T = \sum p_i \dot{q}_i, \quad (3.3.13)$$

where T stands for the kinetic energy and the dot denotes the derivative.

Expressing the kinetic energy in both spherical coordinates and plane polar coordinates, we find that

$$p_r \dot{r} + p_\theta \dot{\theta} + p_\phi \dot{\phi} = p_r \dot{r} + p_\psi \dot{\psi} \quad (3.3.14)$$

where ψ is the plane azimuth angle and p is the corresponding canonical momentum. Hence $p_\theta d\theta$ in eq.(3.3.11) can be replaced by $p d\psi - p_\phi d\phi$ and the action integral becomes

$$I_\theta = \frac{1}{2\pi} \left[\oint p d\psi - \oint p_\phi d\phi \right] \quad (3.3.15)$$

As θ goes through a complete cycle of libration ϕ and ψ vary by 2π and the integration reduces to

$$I_\theta = p - p_\phi = \beta_\theta - \beta_\phi \quad (3.3.16)$$

It is noted that p is equal to β_θ because both quantities are the whole angular dependences in the plane polar coordinates and the spherical coordinates respectively.

We define a radial "action defect", $\delta I(E)$, by writing

$$I_r(E) = I_r^{\text{Coul}}(E) + \delta I(E) \quad (3.3.17)$$

where
$$I_{\lambda}^{\text{Coul}}(E) = \frac{1}{2\pi} \oint_{C_2} \left[2m \left(E + \frac{ze^2}{\lambda} \right) - \frac{\beta_{\theta}^2}{\lambda^2} \right]^{1/2} d\lambda \quad (3.3.18)$$

Z in eq.(3.3.18) is equal to unity for a hydrogen-like atom and C_2 is the classical trajectory appropriate to the pure coulomb field. Integrating $I_{\lambda}^{\text{Coul}}(E)$ and solving eq.(3.3.18) for E , we find

$$E = - \frac{z^2 m e^4}{2 [I_{\lambda}(E) + I_{\theta}(E) + I_{\phi}(E) - \delta I(E)]^2} \quad (3.3.19)$$

This equation can be verified by starting with the integration formula given by Sommerfeld(1928) :

$$J_{\lambda} = \oint \left(A + \frac{2B}{\lambda} - \frac{C}{\lambda^2} \right)^{1/2} d\lambda = 2\pi i \left[\sqrt{-C} + \frac{B}{\sqrt{A}} \right] \quad (3.3.20)$$

From eqs.(3.3.10) and (3.3.11) we have

$$\beta_{\theta}^2 = (I_{\theta} + I_{\phi})^2 \quad (3.3.21)$$

The integral in eq.(3.3.18) can be performed by setting

$$A = 2mE, \quad B = mze^2, \quad C = \beta_{\theta}^2 = (I_{\theta} + I_{\phi})^2 \text{ and then}$$

$$J_{\lambda}^{\text{Coul}} = 2\pi i \left[\sqrt{-(I_{\theta} + I_{\phi})^2 + mze^2} + \frac{mze^2}{\sqrt{2mE}} \right] \quad (3.3.22)$$

Since $J_{\lambda}^{\text{Coul}}(E) = 2\pi I_{\lambda}^{\text{Coul}}$, the above equation can be solved directly for E and it is found that

$$E = - \frac{z^2 m e^4}{2 (I_{\lambda}^{\text{Coul}} + I_{\theta} + I_{\phi})^2}$$

or
$$E = - \frac{z^2 m e^4}{2 [I_{\lambda}(E) + I_{\theta}(E) + I_{\phi}(E) - \delta I(E)]^2} \quad (3.3.23)$$

which is
$$E = - \frac{z^2 m e^4}{2 [n\hbar - \delta I(E)]^2} \quad (3.3.24)$$

if the Bohr-Sommerfeld quantization condition

$$I_r(E) + I_\theta(E) + I_\phi(E) = n\hbar, \quad n = 1, 2, 3, \dots \quad (3.3.25)$$

is applied to eq.(3.3.24).

Eq.(3.3.24) can be rewritten as

$$E = -\frac{Zme^4}{2\hbar^2 [n - \mu_\ell(E)]^2} \quad (3.3.26)$$

provided that

$$\mu_\ell(E) = \delta I(E)/\hbar \quad (3.3.27)$$

The quantum defect, $\mu_\ell(E)$, can then be obtained directly from the equation

$$\mu_\ell(E) \equiv \frac{1}{\hbar} \left\{ \frac{1}{2\pi} \oint_{C_1} (2m[E - V(r)] - \frac{\hbar^2(\ell + 1/2)^2}{r^2})^{1/2} dr - \frac{1}{2\pi} \oint_{C_2} (2m[E + \frac{Ze^2}{r}] - \frac{\hbar^2(\ell + 1/2)^2}{r^2})^{1/2} dr \right\} \quad (3.3.28)$$

where C_1 is the classical trajectory appropriate to the potential field. It is noted that β_θ has been set equal to $(\ell + 1/2)\hbar$ since the quantization of I_ϕ and I_θ gives

$$I_\phi + I_\theta = \beta_\theta = (n_\phi + n_\theta + \frac{1}{2})\hbar \quad (3.3.29)$$

and $I_\phi + I_\theta$ corresponds to the total angular momentum ℓ (Goldstein, 1959).

Eq.(3.3.28) is the required relation between the quantum defect and the potential $V(r)$ and it can be transformed to the atomic unit by introducing :

$$\left. \begin{aligned}
 Q(\rho) &= -\frac{a\rho^2 V(r)}{e^2} = \alpha\rho^2 + \beta\rho + \gamma, \\
 P_{nl}(\rho) &= \frac{1}{2}\epsilon_{nl}\rho^2 + \frac{1}{2}(\ell + \frac{1}{2})^2, \\
 Q^*(\rho) &= -\frac{a\rho^2(-Ze^2)}{e^2 r} = Z\rho, \\
 \text{and } E &= -\epsilon_{nl} \frac{e^2}{2a}
 \end{aligned} \right\} (3.3.30)$$

where ϵ_{nl} is the positive energy of any state in rydberg unit
 (1 rydberg equals 13.6 electron-volts),

$a = \hbar^2/m_e^2$ is the ground-state radius of hydrogen atom ,

and $Q(\rho)$ is an arbitrary function expressed in parabolic form of ρ
 which describes the radial potential , for hydrogen atom

$Q(\rho) = \rho$ overall regions.

The transformed relation is

$$\mu(E) = \frac{\sqrt{2}}{\pi} \left[\int_{\rho_1}^{\rho_2} \sqrt{Q(\rho) - P_{nl}(\rho)} \frac{d\rho}{\rho} - \int_{\rho_3}^{\rho_4} \sqrt{Q^*(\rho) - P_{nl}(\rho)} \frac{d\rho}{\rho} \right] \quad (3.3.31)$$

where ρ_1, ρ_2 and ρ_3, ρ_4 are the classical turning points of the
 two integrals respectively.

The energy levels of an alkali atom can then be found from the
 equation

$$\epsilon_{nl} = \frac{1}{\left[n - \frac{\mu(E)}{\ell} \right]^2} \quad (3.3.32)$$