CHAPTER IV

THE ENERGY SPECTRUM OF HYDROGEN ATOM

In this chapter the energy spectrum of the hydrogen atom will be considered from the exact Green's function. For the two dimensional Green's function, after carrying out the σ-integration we can get the discrete energy spectrum from the poles of the gamma function. In three dimensions, the procedure is rather complicated, we must carry out the double integrations, first,the integration over ξ_N and then over σ. By using the transformation from Kustaanheimo-Stiefel coordinates into four dimensional polar coordinates we can perform these integrations and obtain the Green's function in a closed form. Analogy with the two dimensions, the gamma function will occur as a factor of the Green's function. The appearance of the poles of the gamma function will represent the discrete energy spectrum of the hydrogen atom which equivalents to the Bohr's formula for the energy levels of the hydrogen atom.

4.1 The Energy Spectrum of Hydrogen Atom from the two Dimensional Green's Function.

Consider the Green's function

$$G(\vec{x}'',\vec{x}';E) = \int_0^\infty e^{\frac{ie^2\sigma}{\hbar}} Q(\vec{u}'',\vec{u}';\sigma)\, d\sigma \qquad (4.1)$$

where

$$Q(\vec{u}'',\vec{u}';\sigma) = \frac{M\omega}{8\pi i\hbar}\operatorname{cosec}(\omega\sigma)$$

$$\cdot \exp\left\{ \frac{iM\omega}{2\hbar}\left[(\vec{u}''^2+\vec{u}'^2)\cot(\omega\sigma) - 2\vec{u}'\cdot\vec{u}''\operatorname{cosec}(\omega\sigma)\right]\right\} \quad (4.2)$$

To carry out the σ -integration with the integrals (4.2) we make the σ -integration easier by trying to transform the parabolic variables (u^1, u^2) into polar variables (r, ϕ). By using the transformaing relation

$$\begin{pmatrix} u^1 \\ u^2 \end{pmatrix} = \begin{pmatrix} r^{1/2}\cos\phi/2 \\ r^{1/2}\sin\phi/2 \end{pmatrix} \quad (4.3)$$

it is obvious that

$$\vec{u}''^2 + \vec{u}'^2 = r' + r'' \quad (4.4)$$

$$\vec{u}'\cdot\vec{u}'' = (r'r'')^{1/2}\cos(\phi''-\phi')/2 \quad (4.5)$$

In polar coordinates, therefore the Green's function (4.1) becomes

$$G(r'',\phi'';r',\phi';k) = \frac{2m}{\pi i\hbar}\int_0^\infty \exp\left\{-\frac{2me^2}{i\hbar k}\right\}\operatorname{cosech}q$$

$$\cdot \exp\left\{ik\left[(r'+r'')\coth q - 2(r'r'')^{1/2}\cos(\phi''-\phi')\operatorname{cosech}q\right]\right\}dq \quad (4.6)$$

where $\omega\sigma = iq$ (4.7)

and $k = \left(\frac{2mE}{\hbar}\right)^{1/2} = -i\left(\frac{2m\omega}{\hbar}\right)$, (4.8)

By using the half-angle expansion formular (7),

$$\exp(iz\phi/2) = \sum_{l=-\infty}^{\infty} \exp(il\phi)\, i^{2l} J_{2l}(z) \tag{4.9}$$

the last exponential factor on the right hand side of (4.6) leads

$$G(r'',\phi'';r',\phi';k) = \frac{2m}{\pi i\hbar} \sum_{l=-\infty}^{\infty} i^{2l} e^{il(\phi''-\phi')} \int_0^{\infty} \exp\left\{ \frac{2ime^2 g}{k\hbar^2} \right\} \operatorname{cosech} q$$

$$\cdot \exp\{ik(r'+r'')\coth q\}\, J_{2l}\left[-2k(r'r'')^{1/2} \operatorname{cosech} q\right] dq \tag{4.10}$$

Fortunately the integral in (4.10) can be analytically evaluated by using the following formula (11)

$$\int e^{-2pq} \operatorname{cosech} q \exp\left\{ \frac{(x-y)}{2} \coth q \right\} J_{2\nu}\left[(xy)^{1/2} \operatorname{cosech} q\right] dq$$

$$= (xy)^{-1/2} \frac{\Gamma(p+\nu+1/2)}{\Gamma(2\nu+1)} M_{p,\nu}(x)\, W_{-p,\nu}(y) \tag{4.11}$$

where $M_{p,\nu}(x)$, $W_{p,\nu}(x)$ are the Wittaker's functions of the first and the second kind respectively. As a result, the Green's function (4.10) can be written in the form

$$G(r'',\phi'';r',\phi';k) = \sum_{l=-\infty}^{\infty} \exp\{il(\phi''-\phi')\}\, G_l(r'',r';k) \tag{4.12}$$

with the radial Green's function

$$G_l(r'',r',k) = \frac{m}{k\pi\hbar} i^{2l+1} (r'r'')^{1/2} \frac{\Gamma(p+l+1/2)}{\Gamma(2l+1)} M_{p,l}(2ikr')W_{-p,l}(-2ikr'') \tag{4.13}$$

where
$$p = -\frac{ime^2}{k\hbar^2} = \frac{-me^2}{(2mE\hbar^2)^{1/2}} \tag{4.14}$$

Consider the gamma function $\Gamma(z)$, from the Euler's formula (12) the gamma function is written in the form

$$\Gamma(z) = \lim_{n\to\infty} \frac{n!\,n^z}{z(z+1)(z+2)\cdots\cdots(z+n)} \tag{4.15}$$

The poles of this gamma function occurs when $z = 0, -1, -2, -3, \ldots$ Thus, the discrete energy spectrum of the hydrogen atom can be found from the poles of the gamma function $\Gamma(p + l + \frac{1}{2})$ in (4.13). The poles occur for $p + l + \frac{1}{2} = -n'$ (where $n' = 0, 1, 2\ldots$) which correspond to the discrete energy levels

$$E_n = \frac{-me^4}{2\hbar^2(n+1/2)^2} \tag{4.16}$$

where $n = n' + l = 0, 1, 2, \ldots$

4.2 The Four Dimensional Polar Coordinates

By transforming the Coulomb path integral into an oscillator path integral, the path integration for (3.36) has been completed. In order to arrive at the closed form of the Green's function, two more integrations must be performed. The first integration is to project the oscillator propagator obtained in the Kustaanheimo-Stiefel variables back in to the three dimensional physical space, by eliminating the auxiliary variable ξ . The last step of the procedure is the inverse Fourier transformation (3.47) over σ to find the Coulomb Green's function in the energy domain.

Here, the first integration over ξ will be considered. The integral (3.40) is nontrivial. The trelationship between the u variable and ξ variable will be clarified. For this purpose, the four dimensional polar coordinates $(r, \theta, \phi, \alpha)$ are useful. In term of polar coordinates, the Kustaanheimo-Stiefel coordinates are given by (5),

$$\begin{pmatrix} u^1 \\ u^2 \\ u^3 \\ u^4 \end{pmatrix} = r^{1/2} \begin{pmatrix} \sin\theta/2 \cos(\alpha+\phi)/2 \\ \sin\theta/2 \sin(\alpha+\phi)/2 \\ \cos\theta/2 \cos(\alpha-\phi)/2 \\ \cos\theta/2 \sin(\alpha-\phi)/2 \end{pmatrix} \qquad (4.17)$$

The use of (4.17) in (3.17) yields the familaiar relation

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} r\sin\theta\cos\phi \\ r\sin\theta\sin\phi \\ r\cos\theta \end{pmatrix} \qquad (4.18)$$

which indicates that (r, θ, ϕ) are the usual three dimensional polar variables. The additional angular parameter α describes an extra degree of freedom.

In polar coordinates, the u-dependent terms in (3.42) are expressed as

$$\vec{u}'^2 + \vec{u}''^2 = r' + r'' \tag{4.19}$$

and

$$\vec{u}'\cdot\vec{u}'' = (r'r'')^{1/2}\{\sin\theta'/_2\sin\theta''/_2\cos(\phi''-\phi'+\alpha''-\alpha')/2$$

$$+\cos\theta'/_2\cos\theta''/_2\cos(\phi''-\phi'-\alpha''+\alpha')/2\} \tag{4.20}$$

Notice that (4.20) is the only term that contains the extra anagular parameter α . In eliminating the α - dependence, it is important to use the relationship between the integration variable ξ and the extra parameter α . From (3.29) or (3.30)

$$\xi_N = -u^1_N u^2_{N-1} + u^2_N u^1_{N-1} - u^4_N u^3_{N-1} + u^3_N u^4_{N-1} \tag{4.21}$$

its differential takes the form

$$d\xi_N = -u^2_N du^1_{N-1} + u^1_N du^2_{N-1} - u^4_N du^3_{N-1} + u^3_N du^4_{N-1} \tag{4.22}$$

In the limit $N\rightarrow\infty$ (i.e. $N-1 \rightarrow N$)

$$d\xi_N = -u^2_N du^1_{N-1} + u^1_N du^2_N - u^4_N du^3_N + u^3_N du^4_N \tag{4.23}$$

Utilizing (4.17) in (4.23) , one finds

$$d\xi_N = d\xi'' = r''d\alpha'' - r''\cos\theta'' d\phi'' \tag{4.24}$$

Since (r'', θ'', ϕ'') indicates the end point of the system, it is evident that $d\theta'' = 0$. Consequently (4.24) becomes

$$d\xi'' = r'' d\alpha'' \tag{4.25}$$

Now, substituting of (4.19), (4.20) and (4.25) into (3.40), the result is

$$\begin{aligned} Q(\vec{x}'',\vec{x}';\sigma) = {} & 2^{-4} F^{4}(\sigma) \exp\{-\pi F^{2}(\sigma)(r'+r'')\cos(\omega\sigma)\} \\ & \int_0^{4\pi} \exp\{2\pi F^{2}(\sigma)(r' r'')^{1/2} \sin\theta'/_2 \sin\theta''/_2 \cos[(\phi''-\phi'+\alpha''-\alpha')/2]\} \\ & \exp\{2\pi F^{2}(\sigma)(r'r'')^{1/2} \cos\theta'/_2 \cos\theta''/_2 \cos[(\phi''-\phi'-\alpha''-\alpha')/2]\}\, d\alpha'' \end{aligned} \tag{4.26}$$

It is not too difficult to perform the integration over α''. The expansion formula (5),

$$\exp(z\cos\phi) = \sum_{m=-\infty}^{\infty} \exp(im\phi) I_m(z) \tag{4.27}$$

may be used to rewrite (4.26) as

$$\begin{aligned} Q(\vec{x}'',\vec{x}';\sigma) = {} & 2^{-4} F^{4}(\sigma) \exp\{-\pi F^{2}(\sigma)(r'+r'')\cos(\omega\sigma)\} \\ & \sum_{m}\sum_{m'} I_m(z) I_{m'}(z') \exp\{i(m+m')(\phi''-\phi')/2\} \\ & \exp\{i(m'-m)\tfrac{\alpha'}{2}\} \int_0^{4\pi} \exp\{i(m-m')\tfrac{\alpha''}{2}\}\, d\alpha'' \end{aligned} \tag{4.28}$$

where

$$z = 2\pi F^{2}(\sigma)(r'r'')^{1/2} \sin\theta'/_2 \sin\theta''/_2 \tag{4.29}$$

$$z' = 2\pi F^{2}(\sigma)(r'r'')^{1/2} \cos\theta'/_2 \cos\theta''/_2 \tag{4.30}$$

The α'' - integration in (4.28) is trivial

$$\int_0^{4\pi} \exp\{i(m-m')\tfrac{\alpha''}{2}\}\, d\alpha'' = 4\pi\,\delta(m-m') \tag{4.31}$$

After the α''-integration and the m' - summation, (4.28) is simplified as

$$Q(\vec{x}'',\vec{x}';\sigma) = 2^{-2}\pi F^{4}(\sigma)\exp\{\pi F^{2}(\sigma)(r'+r'')\cos(\omega\sigma)\} \cdot$$

$$\sum_{m} I_{m}(z)I_{m}(z')\exp\{im(\phi''-\phi')\} \qquad (4.32)$$

The expansion formula for the Bessel function of the zeroth order (5),

$$I_{0}[(z^{2}+z'^{2}+2zz'\cos\phi)^{1/2}] = \sum_{m} e^{im\phi} I_{m}(z)I_{m}(z') \qquad (4.33)$$

is immediately applicable to (4.32), reducing (4.32) to the form

$$Q(\vec{x}'',\vec{x}';\sigma) = 2^{-2}\pi F^{4}(\sigma)\exp\{-\pi F^{2}(\sigma)(r'+r'')\cos(\omega\sigma)\}$$

$$\cdot I_{0}[2\pi F^{2}(\sigma)(r'r'')^{1/2}\cos\gamma/2] \qquad (4.34)$$

where
$$\cos^{2}\gamma/2 = \cos^{2}\theta'/2\cos^{2}\theta''/2 + \sin^{2}\theta'/2\sin^{2}\theta''/2$$

$$+ 2\cos\theta'/2\cos\theta''/2\sin\theta'/2\sin\theta''/2\cos(\phi''-\phi'). \qquad (4.35)$$

Thus, the Coulomb propagator on σ -evalution has been in a closed form.

4.3 The Coulomb Green's Function and the Energy Spectrum.

The final step for calculating the Coulomb Green's function is to perform the Fourier integration over σ ,

$$G(\vec{x}'',\vec{x}';E) = \frac{\pi}{4}\int_0^\infty \exp\left(\frac{ie^2\sigma}{\hbar}\right)F^4(\sigma)\exp\{-\pi F^2(\sigma)v\cos(\omega\sigma)\}\cdot$$

$$\cdot I_0[\pi F^2(\sigma)u]\,d\sigma \tag{4.36}$$

where $$u = 2(r'r'')^{1/2}\cos\gamma/2 \tag{4.37}$$

and $$v = r' + r'' \tag{4.38}$$

At this moment, it may be helpful to recall that

$$\omega = (-E/2m)^{1/2} = ik\hbar/2m \tag{4.39}$$

$$F(\sigma) = [4m\omega/2\pi i\hbar\sin(\omega\sigma)]^{1/2} \tag{4.40}$$

Substituting (4.39) into (4.40) yields

$$F^2(\sigma) = \frac{k}{\pi i}\operatorname{cosech}(k\hbar\sigma/2m) \tag{4.41}$$

If the differentiation formula relating the Bessel function of the zeroth order and the first order (13)

$$auI_0(au) = \frac{d}{du}(uI_1(au)) \tag{4.42}$$

is used, then (4.36) can be put into an integral form

$$G(\vec{x}'',\vec{x}';E) = \frac{k}{4\pi i u}\frac{d}{du}\Big\{u\int_0^\infty \exp(ie^2\sigma/\hbar)\ \text{cosech}(k\hbar\sigma/2m)$$

$$\cdot\exp\{ikv\coth(k\hbar\sigma/2m)\}I_1[-iku\,\text{cosech}(k\hbar\sigma/2m)]\,d\sigma\Big\} \qquad (4.43)$$

Notice that from (4.35), (4.36) and (4.38)

$$v^2 - u^2 = (r' + r'')^2 - 4r'r''\cos^2\gamma/2$$

$$= r'^2 + r''^2 - 2r'r''\cos\gamma$$

$$= |\vec{x}'' - \vec{x}'|^2 \qquad (4.44)$$

where $\cos\gamma = \cos\theta'\cos\theta'' + \sin\theta'\sin\theta''\cos(\phi'' - \phi')$ (4.45)

Then, define

$$a = r' + r'' - |\vec{x}'' - \vec{x}'| = v - (v^2 - u^2)^{1/2} \qquad (4.46)$$

$$b = r' + r'' + |\vec{x}'' - \vec{x}'| = v + (v^2 - u^2)^{1/2} \qquad (4.47)$$

and recognize that u and v can be expressed as

$$u = (ab)^{1/2} \qquad (4.48)$$

$$v = \frac{(a + b)}{2} \qquad (4.49)$$

It is now possible to employ the integral formula

$$\int_0^{\infty} e^{-2pq}\,\mathrm{cosech}\,q\,\exp\{(\tfrac{x-y}{2})\coth q\}\,J_{2t}((xy)^{1/2}\mathrm{cosech}\,q)\,dq$$

$$= (xy)^{-1/2}\frac{\Gamma(p+t+1/2)}{\Gamma(2t+1)} M_{p,t}(x)\,W_{-p,t}(y) \tag{4.50}$$

for completing the σ - integration of (4.43) . Setting $q = \frac{k\hbar\sigma}{2m}$

$P = -\frac{ime^2}{k\hbar^2}$, $x = ika$, $y = -ikb$ and $t = \frac{1}{2}$ results in the form

$$G(\vec{x}'',\vec{x}';E) = -\frac{m}{2\pi k\hbar u}\Gamma(p+1)\frac{\partial}{\partial u}\Big[M_{p,1/2}(ika)\,W_{-p,1/2}(-ikb)\Big] \tag{4.51}$$

or using the Kummer transformation (14)

$$M_{p,m}(z) = (-1)^{-m-1/2} M_{-p,m}(-z) \tag{4.52}$$

then

$$G(\vec{x}'',\vec{x}';E) = \frac{m}{2\pi\hbar ku}\Gamma(p+1)\frac{\partial}{\partial u}\Big[M_{-p,1/2}(-ika)\,W_{-p,1/2}(-ikb)\Big] \tag{4.53}$$

Upon differentiation, the Green's function (4.53) is given in a closed form

$$G(\vec{x}'',\vec{x}';E) = \frac{im\Gamma(p+1)}{2\pi\hbar|\vec{x}''-\vec{x}'|}\det\begin{vmatrix} M_{-p,1/2}(-ika) & W_{-p,1/2}(-ikb) \\ M'_{-p,1/2}(-ika) & W'_{-p,1/2}(-ikb) \end{vmatrix} \tag{4.54}$$

where $M'_{\kappa,\mu}(z) = \frac{\partial M_{\kappa,\mu}(z)}{\partial z}$; $W'_{\kappa,\mu}(z) = \frac{\partial W_{\kappa,\mu}(z)}{\partial z}$ (4.55)

The result (4.54) is the same form as that obtained by Hostler (15) without using the path integral. The energy eigenvalues correspond to the poles of $\Gamma(P + 1)$ which occur when $P = -n$ $(n = 1, 2, \ldots)$. Since $P = -\frac{ime^2}{k\hbar^2}$ and $k\hbar = (2mE)^{\frac{1}{2}}$, the energy spectrum is given by

$$E_n = -\frac{me^4}{2\hbar^2 n^2} \qquad (4.56)$$

which is the well-known result.