CHAPTER V

THE WAVE FUNCTIONS OF HYDROGEN ATOM

In this chapter, we will show how to derive the wave functions from the Coulomb Green's function obtained in chapter IV. The residues of the Green's function which represent the wave functions (or eigen functions) in general can be found for any n^{th} eigen state. Here, we will determine the ground state, the first two excited state and the general n^{th} eigen state of the hydrogen atom in three dimensions.

5.1 The Eigen Function Expansion of the Green's Function.

Now, consider the wave function (1.5)

$$\Psi(\vec{x}'',t'') = \int_{-\infty}^{\infty} K(\vec{x}'',\vec{x}';t'',t')\Psi(\vec{x}',t')\, d^3x' \tag{5.1}$$

Since the wave function can be written as an eigen function expansion (15)

$$\Psi(\vec{x}'',t'') = \sum_{n=1}^{\infty} C_n \Psi_n(\vec{x}'',t'')$$

$$= \sum_{n=1}^{\infty} C_n \Psi_n(\vec{x}')e^{-\frac{i}{\hbar}E_n t''} \tag{5.2}$$

and

$$\Psi(\vec{x}',t') = \sum_{n=1}^{\infty} C_n \Psi_n(\vec{x}')e^{-\frac{i}{\hbar}E_n t'} \tag{5.3}$$

The coefficient C_n can be evaluated,

$$C_n = \int_{-\infty}^{\infty} \psi_n^*(\vec{x}')\psi(\vec{x}',t')e^{\frac{i}{\hbar}E_n t'} d^3x' \tag{5.4}$$

Then, substituting C_n into (5.2), the wave function $\psi(\vec{x}'', t'')$ becomes

$$\psi(\vec{x}'',t'') = \int_{-\infty}^{\infty} \sum_{n=1}^{\infty} \psi_n(\vec{x}'')\psi_n^*(\vec{x}')e^{-\frac{i}{\hbar}E_n(t''-t')}\psi(\vec{x}',t')d^3x' \tag{5.5}$$

Comparing (5.5) to (5.1), we obtain

$$K(\vec{x}'',\vec{x}';t'',t') = \sum_{n=1}^{\infty} \psi_n(\vec{x}'')\psi_n^*(\vec{x}')e^{-\frac{i}{\hbar}E_n(t''-t')} \tag{5.6}$$

If we take a Fourier transform to the propagator (5.6), we obtain the Green's function

$$G(\vec{x}'',\vec{x}';E) = \int_{0}^{\infty} K(\vec{x}'',\vec{x}';t'',t')e^{\frac{i}{\hbar}E(t''-t')}d(t''-t')$$

$$= i\hbar \sum_{n=1}^{\infty} \frac{\psi_n(\vec{x}'')\psi_n^*(\vec{x}')}{E-E_n} \tag{5.7}$$

From (5.6) and (5.7), we find that the propagator and the Green's function give us the knowledge of both the energy spectrum and the wave function simultaneously. The last section of this chapter we will determine the wave functions from the Coulomb Green's function (4.54).

5.2 The Wave Function of Hydrogen Atom in Three Dimensions.

It is wellknown that if the total Hamiltonian of the system is given, one could set up an eigen value equation to derive its energy spectrum or construct a wave equation to derive its probability amplitude. For the hydrogen atom problem, one knows that the wave function (or eigen function) depends on the quantum number n, ℓ and m, namely, $\psi_{n\ell m}(r)$ the usual spherical wave function of the hydrogen atom can be written in the form (8)

$$\psi_{n\ell m}(\vec{r}) = \frac{1}{\sqrt{\pi}\, n}\left(\frac{me^2}{n\hbar^2}\right)^{3/2} \sqrt{\frac{(2\ell+1)(\ell-|m|)!\,(n-\ell-1)!}{(\ell+|m|)!\,(n+\ell)!}}\; e^{jm\phi} P_\ell^m(\cos\theta)$$

$$\cdot\left(\frac{2me^2r}{n\hbar^2}\right)^{\ell} e^{-\frac{me^2}{n\hbar^2}r} L_{n-\ell-1}^{2\ell+1}\left(\frac{2me^2}{n\hbar^2}r\right) \qquad (5.8)$$

where $P_\ell^m(x)$ and $L_n^\alpha(x)$ are the associated Legendre function and Laquerre function respectively. The principal quantum number n relates to the energy level as

$$E_n = -\frac{me^4}{2\hbar^2 n^2}, \quad n = 1, 2, 3, \ldots \qquad (5.9)$$

When n is given, ℓ and m can be found from the following rules:

for the restrictive n

ℓ can be $n-1, n-2, \ldots 3, 2, 1, 0$

m can be $-(n-1), -(n-2), \ldots 0 \ldots (n-2), (n-1)$.

We find that each given value of ℓ, there are $2\ell+1$ values of m, so that the number of degenerate states can be evaluated from the formula

$$N = \sum_{l=0}^{n-1} (2l+1) = n^2 . \tag{5.10}$$

5.3 The Ground State and Excited State Wave Functions of Hydrogen Atom from Coulomb Green's Function.

Here, we willl determine the wave function of the hydrogen atom from the exact Green's function (4.54)

$$G(\vec{x}'',\vec{x}';E) = \frac{im\,\Gamma(p+1)}{2\pi\hbar\,|\vec{x}''-\vec{x}'|}\ \det \begin{vmatrix} M_{-p,1/2}(-ika) & W_{-p,1/2}(-ikb) \\ M'_{-p,1/2}(-ika) & W'_{-p,1/2}(-ikb) \end{vmatrix} \tag{5.11}$$

Considering the Green's function in (5.7) , its residues represent the wave functions of the quantized system. For the n^{th} eigen state, the residue $\psi_n^*(\vec{x}')\psi_n(\vec{x}'')$ can be found from the following formula (17)

$$\mathrm{Res}\,G(\vec{x}'',\vec{x}';E) = \lim_{E\to E_n} (E-E_n)\,G(\vec{x}'',\vec{x}';E) = i\hbar\,\psi_n(\vec{x}'')\psi_n^*(\vec{x}') \tag{5.12}$$

Similarly, the Coulomb Green's function in (5.11) satisfies this property, namely, one can verify that $\psi_{nlm}(\vec{r})$ can be found by using equation (5.12). Because of its degeneracy, it is too difficult to derive the wave function of the hydrogen atom from the residue of $G(\vec{x}'', \vec{x}', E)$ for the general n^{th} eigen state. Here, we will show how to derive the wave function of the hydrogen atom from the residue of $G(\vec{x}'',\vec{x}'';E)$ for $n = 1, 2, 3$ and for general n respectively. Now we consider the residue of Coulomb Green's function for general n, the energy level is

$$E_n = -\frac{me^4}{2\hbar^2 n^2} \tag{5.13}$$

From (5.11) the residue of $G(\vec{x}'', \vec{x}'; E)$ becomes

$$\mathrm{Res}\, G(\vec{x}'',\vec{x}';E) = \lim_{E\to E_n}(E-E_n)\frac{im\,\Gamma(p+1)}{2\pi\hbar\,|\vec{x}''-\vec{x}'|}\det\begin{vmatrix} M_{-p,1/2}(-ika) & W_{-p,1/2}(-ikb) \\ M'_{-p,1/2}(-ika) & W'_{-p,1/2}(-ikb)\end{vmatrix} \qquad (5.14)$$

Recognizing that $P = -\frac{ime^2}{k\hbar^2}$ and $k = (\frac{2mE}{\hbar^2})^{\frac{1}{2}}$, so that when the limit $E \longrightarrow E_n$ is taken,

$$P = -\frac{ime^2}{k\hbar^2} \longrightarrow -n ,$$

$$\text{and} \quad k = (\frac{2mE}{\hbar^2})^{\frac{1}{2}} \longrightarrow \frac{ime^2}{n\hbar^2} .$$

Upon using the relation (18)

$$\Gamma(P+1) = \frac{\Gamma(P+n+1)}{(P+1)(P+2)\ldots(P+n)} \qquad (5.15)$$

and substituting $E = -\frac{me^4}{2\hbar^2 n^2}$ into (5.14), (5.14) becomes

$$\mathrm{Res}\, G(\vec{x}'',\vec{x}';E) = \frac{im\,(-1)^n}{\pi n\hbar\,(n-1)!}\left(\frac{me^4}{2\hbar^2 n^2}\right)\frac{1}{|\vec{x}''-\vec{x}'|}\left\{M_{n,1/2}(-ika)W'_{n,1/2}(-ikb)-W_{n,1/2}(-ikb)M'_{n,1/2}(-ika)\right\} \qquad (5.16)$$

For convenient we set $-ika = z$ and $-ikb = z'$. Then using the transformation (18)

$$zM'_{k,\mu}(z) = (z/2-k)M_{k,\mu}(z) + (1/2+k+\mu)M_{k+1,\mu}(z) ,$$

$$\qquad (5.17)$$

$$zW'_{k,\mu}(z) = (z/2-k)W_{k,\mu}(z) - W_{k+1,\mu}(z)$$

and

$$
\begin{aligned}
M_{\kappa,\mu}(z) &= e^{\frac{1}{2}z} z^{\frac{1}{2}+\mu} M(\tfrac{1}{2}+\mu-\kappa, 1+2\mu, z) \\
W_{\kappa,\mu}(z) &= e^{\frac{1}{2}z} z^{\frac{1}{2}+\mu} U(\tfrac{1}{2}+\mu-\kappa, 1+2\mu, z)
\end{aligned} \tag{5.18}
$$

to transform (5.16) into the form

$$
\begin{aligned}
\operatorname{Res} G(\vec{x}'', \vec{x}'; E) = {} & \frac{im(-1)^n}{\pi n\hbar (n-1)!} \left(\frac{me^4}{2n^2\hbar^2}\right) \frac{e^{-\frac{1}{2}(z+z')}}{|\vec{x}''-\vec{x}'|} \Big\{ n(z-z') M(-(n-1),2,z) U(-(n-1),2,z') \\
& - z' M(-n,2,z) U(-(n-1),2,z') + z M(-(n-1),2,z) U(-n,2,z') \Big\}
\end{aligned} \tag{5.19}
$$

If the transformation (18)

$$
\begin{aligned}
M(-n, (\alpha+1), z) &= \frac{n!}{(\alpha+1)_n} L_n^{\alpha}(z) \\
U(-n, (\alpha+1), z) &= n! (-1)^n L_n^{\alpha}(z)
\end{aligned} \tag{5.20}
$$

is employed, then (5.19) can be put into the form

$$
\begin{aligned}
\operatorname{Res} G(\vec{x}'', \vec{x}'; E) = {} & \frac{im(-1)^n}{\pi n\hbar (n-1)!} \left(\frac{me^4}{2n^2\hbar^2}\right) \frac{e^{-\frac{1}{2}(z+z')}}{|\vec{x}''-\vec{x}'|} (n-1)!(-1)^{n-1} \Big\{ z L_{n-1}^{1}(z) L_n^{0}(z') \\
& - z' L_n^{0}(z) L_{n-1}^{1}(z') \Big\}
\end{aligned} \tag{5.21}
$$

After using the transformation (18)

$$
z L_n^{\alpha+1}(z) = (n+\alpha+1) L_n^{\alpha}(z) - (n+1) L_{n+1}^{\alpha}(z) \tag{5.22}
$$

and

$$
\sum_{m=0}^{n} \frac{m!\, L_m^{\alpha}(x) L_m^{\alpha}(y)}{\Gamma(m+\alpha+1)} = \frac{(n+1)!}{\Gamma(\alpha+n+1)(x-y)} \left[L_n^{\alpha}(x) L_{n+1}^{\alpha}(y) - L_{n+1}^{\alpha}(x) L_n^{\alpha}(y) \right] \tag{5.23}
$$

(5.21) becomes

$$\mathrm{Res}\,G(\vec{x}'',\vec{x}';E) = -\frac{im}{\pi n\hbar}\left(\frac{me^4}{2n^2\hbar^2}\right)\frac{(z-z')}{|\vec{x}''-\vec{x}'|}e^{-\frac{1}{2}(z+z')}\sum_{m=0}^{n-1} L_m^0(z)L_m^0(z') \qquad (5.24)$$

Rocognizing that

$$z = -ika = -ik(r'+r''-|\vec{x}''-\vec{x}'|)$$

$$z' = -ikb = -ik(r'+r''+|\vec{x}''-\vec{x}'|) \qquad (5.25)$$

and

$$z-z' = 2ik\,|\vec{x}''-\vec{x}'|$$

$$z+z' = -2ik(r'+r'') \qquad (5.26)$$

$$zz' = 4i^2k^2r'r''\cos^2\gamma/2 = 4i^2k^2r'r''\frac{(\cos\gamma+1)}{2}$$

then using the relation (19)

$$L_n^{\alpha}(x)L_n^{\alpha}(y) = \frac{\Gamma(1+\alpha+n)}{n!}\sum_{m=0}^{n} L_{n-m}^{\alpha+2m}(x+y)\frac{(xy)^m}{m!\,\Gamma(m+\alpha+1)} \qquad (5.27)$$

to transform (5.24) into a useful form

$$\mathrm{Res}\,G(\vec{x}'',\vec{x}';E) = -\frac{im}{\pi n\hbar}\left(\frac{me^4}{2n^2\hbar^2}\right)(2ik)e^{ik(r'+r'')}\sum_{l=0}^{n-1}\sum_{m=0}^{l} L_{l-m}^{2m}(-2ik(r'+r''))(4i^2k^2r'r'')^m\frac{(\cos\gamma+1)^m}{(m!)^2\,2^m} \qquad (5.28)$$

Now we consider the case for $n=1$, at the ground state of the hydrogen atom, (5.28) thus becomes

$$\mathrm{Res}\,G(\vec{x}'',\vec{x}';E) = -\frac{im}{\pi\hbar}\left(\frac{me^4}{2\hbar^2}\right)(2ik)e^{ik(r'+r'')}L_0^0(-2ik(r'+r'')) \qquad (5.29)$$

Recognizing that $k = \frac{ime^2}{h^2}$, then using the formula (19)

$$\overset{\alpha}{L}_n(x) = \sum_{m=0}^{n} (-1)^m \binom{n+\alpha}{n-m} \frac{x^m}{m!} \qquad (5.30)$$

to transform (5.29) into a familiar form

$$\mathrm{Res}\,G(\vec{x}'',\vec{x}';E) = \frac{i\hbar}{\pi}\left(\frac{m^3e^6}{\hbar^6}\right) e^{-\frac{me^2(r'+r'')}{\hbar^2}} \overset{1}{L}_0\left(\frac{2me^2r'}{\hbar^2}\right) \overset{1}{L}_0\left(\frac{2me^2r''}{\hbar^2}\right) \qquad (5.31)$$

Obviously, the factor $\frac{1}{\sqrt{\pi}}\left(\frac{me^2}{\hbar^2}\right)^{3/2} e^{-\frac{me^2r'}{\hbar^2}} \overset{1}{L}_0\left(\frac{2me^2r'}{\hbar^2}\right)$ is the ground state wave function $\psi_{100}(\vec{r}')$ of the hydrogen atom in three dimensions.

For $n = 2$, the first excited state of the hydrogen atom, (5.28) becomes

$$\mathrm{Res}\,G(\vec{x}'',\vec{x}';E) = -\frac{im}{2\pi\hbar}\left(\frac{me^4}{2\hbar^2 2^2}\right)(2ki)\, e^{ik(r'+r'')} \Big\{ \overset{0}{L}_0(-2ik(r'+r'')) + \overset{0}{L}_1(-2ik(r'+r''))$$

$$+ \overset{2}{L}_0(-2ik(r'+r''))(4i^2k^2r'r'')\left(\frac{\cos\gamma+1}{2}\right) \Big\} \qquad (5.32)$$

Again, the formula (5.30) is used to transform (5.32) into the form,

$$\mathrm{Res}\,G(\vec{x}'',\vec{x}';E) = -\frac{mi}{2\pi\hbar}\left(\frac{me^4}{4\hbar^2}\right)(ki)\, e^{ik(r'+r'')} \left\{ \frac{1}{2}\left((2+2kir')(2+2kir'')+(2ki)^2 r''r'\cos\gamma\right)\right\} \qquad (5.33)$$

From (4.45),

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

$$= \cos\theta''\cos\theta' + \frac{1}{2}\left(\sin\theta''\sin\theta'\, e^{i(\phi''-\phi')} + \sin\theta''\sin\theta' e^{-i(\phi''-\phi')}\right)$$

(5.34)

and recognizing that $k = \frac{ime^2}{2h^2}$, so that (5.33) can be written as

$$\mathrm{Res}\,G(\vec{x}'',\vec{x}';E) = \frac{i\hbar}{32\pi}\left(\frac{m^3e^6}{\hbar^6}\right)e^{-\frac{me^2}{2\hbar^2}(r'+r'')}\left\{ L_1^1\left(\frac{me^2}{\hbar^2}r'\right)L_1^1\left(\frac{me^2}{\hbar^2}r''\right)\right.$$

$$+\left(\frac{me^2}{\hbar^2}\right)^2 r'r'' L_0^3\left(\frac{me^2}{\hbar^2}r'\right)L_0^3\left(\frac{me^2}{\hbar^2}r''\right)P_1^0(\cos\theta'')P_1^0(\cos\theta')$$

$$\left.+\left(\frac{me^2}{\hbar^2}\right)^2 r'r'' L_0^3\left(\frac{me^2}{\hbar^2}r'\right)L_0^3\left(\frac{me^2}{\hbar^2}r''\right)\frac{1}{2}\left(P_1^1(\cos\theta'')P_1^1(\cos\theta')e^{i(\phi''-\phi')}+P_1^{-1}(\cos\theta'')P_1^{-1}(\cos\theta')e^{-i(\phi''-\phi')}\right)\right\} \quad (5.35)$$

Comparing between (5.35) and (5.8) gives the residues of the Coulomb Green's function.

$$\mathrm{Res}\,G(\vec{x}'',\vec{x}';E) = i\hbar\left\{\psi_{200}(\vec{r}'')\psi^*_{200}(\vec{r}')+\psi_{210}(\vec{r}'')\psi^*_{210}(\vec{r}')+\psi_{211}(\vec{r}'')\psi^*_{211}(\vec{r}')+\psi_{21-1}(\vec{r}'')\psi^*_{21-1}(\vec{r}')\right\} \quad (5.36)$$

Substituting n = 3 into (5.28), we obtain

$$\mathrm{Res}\,G(\vec{x}'',\vec{x}';E) = -\frac{im}{3\pi\hbar}\left(\frac{me^4}{9\hbar^2}\right)(ik)e^{ik(r'+r'')}\left\{L_0^0(-2ik(r'+r''))+L_1^0(-2ik(r'+r''))\right.$$

$$+L_0^2(-2ik(r'+r''))(4i^2k^2r'r'')\frac{(\cos\gamma+1)}{2}+L_2^0(-2ik(r'+r''))$$

$$\left.+L_1^2(-2ik(r'+r''))(4i^2k^2r'r'')\frac{(\cos\gamma+1)}{2}+L_0^4(-2ik(r'+r''))(4i^2k^2r'r'')^2\frac{(\cos\gamma+1)^2}{4\cdot 4}\right\} \quad (5.37)$$

Upon using the relation (5.30) we can write (5.37) as

$$\mathrm{Res}\,G(\vec{x}'',\vec{x}';E) = -\frac{im}{9\pi\hbar}\left(\frac{me^4}{9\hbar^2}\right)(ik)e^{ik(r'+r'')}\left\{\frac{1}{3}L_2^1(-2ikr')L_2^1(-2ikr'')+2(-2ikr')(-2ikr'')\right.$$

$$-\frac{1}{2}(-2ikr')(-2ikr'')(-2ik)(r'+r'')\;-\frac{1}{12}(-2ikr')^2(-2ikr'')^2$$

$$\left.+\frac{1}{16}(-2ikr')^2(-2ikr'')^2(\cos^2\gamma+2\cos\gamma+1)\right\} \quad (5.38)$$

Considering the terms that contain $\cos\gamma$ as a factor

$$2(-2ikr')(-2ikr'')\cos\gamma - \frac{1}{2}(-2ikr')(-2ikr'')(-2ik)(r'+r'')\cos\gamma + \frac{1}{8}(-2ikr')^2(-2ikr'')^2\cos\gamma$$

$$= \cos\gamma(-2ikr')(-2ikr'')\frac{1}{8}\left(16 - 4(-2ik)(r'+r'') + (-2ikr')(-2ikr'')\right)$$

$$= \cos\gamma(-2ikr')(-2ikr'')\frac{1}{8}L^3_1(-2ikr')L^3_1(-2ikr'') \qquad (5.39)$$

so that (5.38) can be put into the form

$$\operatorname{Res} G(\vec{x}'',\vec{x}';E) = -\frac{im}{3\pi\hbar}\left(\frac{me^4}{9\hbar^2}\right)(ik)e^{ik(r'+r'')}\Big\{\frac{1}{3}L^1_2(-2ikr')L^1_2(-2ikr'')$$

$$+\frac{1}{8}\cos\gamma(-2ik)^2r'r''L^3_1(-2ikr')L^3_1(-2ikr'')+(-2ikr')^2(-2ikr'')^2\frac{1}{16}(\cos^2\gamma-\frac{1}{3})\Big\} \qquad (5.40)$$

Again, the relation $\cos\gamma = \cos\theta''\cos\theta' + \sin\theta''\sin\theta'\cos(\phi''-\phi')$ is used to transform (5.40) into the form

$$\operatorname{Res} G(\vec{x}'',\vec{x}';E) = -\frac{im}{3\pi\hbar}\left(\frac{me^4}{9\hbar^2}\right)(ik)e^{ik(r'+r'')}\Big\{\frac{1}{3}L^1_2(-2ikr')L^1_2(-2ikr'')$$

$$+\frac{1}{8}(4i^2k^2)(r'r'')L^3_1(-2ikr')L^3_1(-2ikr'')(\cos\theta''\cos\theta'+\sin\theta''\sin\theta'\cos(\phi''-\phi'))$$

$$+\frac{1}{16}(4i^2k^2)^2(r'r'')^2\Big(\frac{2}{9}(3\sin\theta''\cos\theta'')(3\sin\theta'\cos\theta')\cos(\phi''-\phi')+\frac{1}{18}(3\sin^2\theta'')(3\sin^2\theta')\cos 2(\phi''-\phi')$$

$$+\frac{2}{3}\left(\frac{3\cos^2\theta''-1}{2}\right)\left(\frac{3\cos^2\theta'-1}{2}\right)\Big)\Big\} \qquad (5.41)$$

Recognizing that $k = \frac{ime^2}{3\hbar^2}$ and $\cos\phi = \frac{e^{i\phi}+e^{-i\phi}}{2}$, so that (5.41) can be written as

$$\mathrm{Res}\,G(\vec{x}'',\vec{x}';E) = \frac{i}{3\pi}\left(\frac{me^6}{27\hbar^5}\right)^3 e^{-\frac{me^2(r'+r'')}{3\hbar^2}} \Big\{ \frac{1}{3} L_2^1\left(\frac{2}{3}\frac{me^2r'}{\hbar^2}\right) L_2^1\left(\frac{2}{3}\frac{me^2r''}{\hbar^2}\right)$$

$$+ \frac{1}{8}\left(\frac{2}{3}\frac{me^2}{\hbar^2}\right)^2 (r'r'') L_1^3\left(\frac{2}{3}\frac{me^2r'}{\hbar^2}\right) L_1^3\left(\frac{2}{3}\frac{me^2r''}{\hbar^2}\right)\Big(P_1^0(\cos\theta'') P_1^0(\cos\theta') + \frac{1}{2}\big(P_1^1(\cos\theta'') P_1^1(\cos\theta') e^{i(\phi''-\phi')} + P_1^{-1}(\cos\theta'') P_1^{-1}(\cos\theta') e^{-i(\phi''-\phi')}\big)$$

$$+ \frac{1}{24}\left(\frac{2}{3}\frac{me^2}{\hbar^2}\right)^4 (r'r'')^2 L_0^5\left(\frac{2}{3}\frac{me^2r'}{\hbar^2}\right) L_0^5\left(\frac{2}{3}\frac{me^2r''}{\hbar^2}\right) P_2^0(\cos\theta'') P_2^0(\cos\theta')$$

$$+ \frac{1}{(9)(16)}\left(\frac{2}{3}\frac{me^2}{\hbar^2}\right)^4 (r'r'')^2 L_0^5\left(\frac{2}{3}\frac{me^2r'}{\hbar^2}\right) L_0^5\left(\frac{2}{3}\frac{me^2r''}{\hbar^2}\right)\Big(P_2^1(\cos\theta'') P_2^1(\cos\theta') e^{i(\phi''-\phi')}$$

$$+ P_2^{-1}(\cos\theta'') P_2^{-1}(\cos\theta') e^{-i(\phi''-\phi')}\Big) + \frac{1}{(18)(32)}\left(\frac{2}{3}\frac{me^2}{\hbar^2}\right)^4 (r'r'')^2 L_0^5\left(\frac{2}{3}\frac{me^2r'}{\hbar^2}\right) \cdot$$

$$L_0^5\left(\frac{2}{3}\frac{me^2r''}{\hbar^2}\right)\Big(P_2^2(\cos\theta'') P_2^2(\cos\theta') e^{2i(\phi''-\phi')} + P_2^{-2}(\cos\theta'') P_2^{-2}(\cos\theta') e^{-2i(\phi''-\phi')}\Big)\Big\} \qquad (5.42)$$

Then, (5.42) can be put into a familiar form

$$\mathrm{Res}\,G(\vec{x}'',\vec{x}';E) = i\hbar\Big\{ \psi_{300}(\vec{r}'')\psi^*_{300}(\vec{r}') + \psi_{310}(\vec{r}'')\psi^*_{310}(\vec{r}') + \psi_{311}(\vec{r}'')\psi^*_{311}(\vec{r}') + \psi_{31-1}(\vec{r}'')\psi^*_{31-1}(\vec{r}')$$

$$+ \psi_{320}(\vec{r}'')\psi^*_{320}(\vec{r}') + \psi_{321}(\vec{r}'')\psi^*_{321}(\vec{r}') + \psi_{32-1}(\vec{r}'')\psi^*_{32-1}(\vec{r}') + \psi_{322}(\vec{r}'')\psi^*_{322}(\vec{r}') + \psi_{32-2}(\vec{r}'')\psi^*_{32-2}(\vec{r}')\Big\} \qquad (5.43)$$

In analogy to the case for n = 1, 2, 3, one can verify that the residues of the Coulomb Green's function (5.28)

$$\mathrm{Res}\,G(\vec{x}'',\vec{x}';E) = -\frac{im}{n\pi\hbar}\left(\frac{me^4}{2\hbar^2 n^2}\right)(2ik)\, e^{ik(r'+r'')} \sum_{l=0}^{n-1}\sum_{m=0}^{l} L_{l-m}^{2m}(-2ik(r'+r''))$$

$$(4i^2k^2r'r'')^m \frac{(\cos\gamma+1)^m}{2^m(m!)^2} \qquad (5.44)$$

can be put into the form

$$\mathrm{Res}\,G(\vec{x}'',\vec{x}';E) = \frac{i\hbar}{\pi n}\left(\frac{me^2}{n\hbar^2}\right)^3 \sum_{\ell=0}^{n-1}\sum_{m=-\ell}^{\ell}\left(\frac{(2\ell+1)(\ell-|m|)!\,(n-\ell-1)!}{(\ell+|m|)!\,(\ell+n)!}\right)$$

$$e^{im(\phi''-\phi')}P_\ell^m(\cos\theta'')P_\ell^m(\cos\theta')\left(\frac{2me^2}{n\hbar^2}\right)^{2\ell}(r'r'')^\ell e^{-\frac{me^2}{n\hbar^2}(r'+r'')}L_{n-\ell-1}^{2\ell+1}\left(\frac{2me^2}{n\hbar^2}r'\right)L_{n-\ell-1}^{2\ell+1}\left(\frac{2me^2}{n\hbar^2}r''\right) \qquad (5.45)$$

or in a less restrictive form

$$\mathrm{Res}\,G(\vec{x}'',\vec{x}';E) = i\hbar\sum_{\ell=0}^{n-1}\sum_{m=-\ell}^{\ell}\psi_{n\ell m}(\vec{r}'')\psi^*_{n\ell m}(\vec{r}') \qquad (5.46)$$

Thus, the Coulomb Green's function give us the knowledge of both the energy levels and the wave functions of the hydrogen atom simultaneously.