# Fourier Transform of Hydrogen Type Atomic Orbitals

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Fourier Transform of Hydrogen Type Atomic Orbitals

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Abstract. Hydrogen type atomic orbitals (HTOs) are important part of other exponential type orbitals (ETOs). These orbitals have some mathematical properties and they are used usually in the theoretical atomic and molecular investigations as special functions to figure out analytical expressions. Fourier transform method (FTM) is a great way to denote basis functions into the momentum space. Because, their Fourier transforms are easier to use in mathematical calculations. In this paper, we obtain new and useful mathematical representations for the Fourier transform of HTOs related with Gegenbauer polynomials and hypergeometric functions, by using recurrence relations of Laguerre polynomials, Rayleigh expansion and some properties of normalized HTOs.

Keywords: Hydrogen type atomic orbitals, Fourier transform, Laguerre polynomials, Hypergeometric functions, Gegenbauer polynomials.

Introduction

In quantum mechanics, theory and application of the hydrogen atom, analytical solutions of the Schrödinger equation, the exact eigenfunctions in the discrete spectrum, mentioned the hydrogen atomic orbitals or hydrogen type functions, play an important role in quantum mechanical applications of atoms, molecules, and also solids [1]. Their significance is owing to the fact that they are a basis functions for quantal calculations of atoms and molecules, such as it was underlined in references [2, 3]. In these studies it was shown that expansions over HTOs appear naturally when one makes an effort the momentum representation of Schrödinger problem for a single electron in a multi-center Coulomb field of nuclei in the any molecule. Some of the other useful studies about using and applications of HTOs as bound states, integral transforms and the analytical expressions for the weight functions can be found separately in the references [4, 5, 6]. Besides, Fourier transforms over hyperspherical harmonics [7] and four-dimensional harmonics and quadratic transformations [8] are other important theoretical studies for HTOs.

Recently, FTM has been used for the evaluation of molecular integrals, and through the agency of this method, multi-center integrals are transformed into the inverse Fourier integrals [9, 10, 11]. In this process, there are unnecessary difficulties for using basis functions, but their Fourier transforms are getting quite big analytical simplicity, namely Fourier transform of HTOs are better than their row forms to evaluate multi-center molecular integrals, especially for overlap integrals. Overlap integrals have intermediate steps for the derivation and calculation of all other multi-center integrals. The evaluation of overlap and other multi-center integrals are already based on ab initio calculations, and there accurate functions are needed to supply the requirements of cusp condition and exponential decay. Theoretical investigations in this field are coming from the early study of Roothaan and Ruedenberg [12, 13, 14], Coulson [15], Löwdin [16], until more recent works by Silverstone [17], Steinborn [18], Jones [19], Rinaldi’s groups [20].
General Properties and Relations

In this part, we will principally introduce general properties for calculation which are needed next steps. The full eigenfunctions of the discrete spectrum for hydrogenic atoms can be shown by [21]

\[ \psi_{nl}^m(\vec{r}) = R_{nl}(r)Y_l^m(\theta, \phi) \] (1)

where, \( n, l, \) and \( m \) quantum numbers, \( Y_l^m(\theta, \phi) \) are spherical harmonics and regular solid harmonics [22]

\[ S_l^m(\vec{r}) = r^l Y_l^m(\theta, \phi) \] (2)

The normalized radial functions in Eq. (1) for the bound states of hydrogenic atoms are given as [21]

\[ R_{nl}(r) = \left( \frac{2}{n}\right)^{1/2} \frac{(n-1)!}{2n[(n+l)!]^2} r^{l+1/2} e^{-\rho^2/4} \lambda_{nl}^m(r) \] (3)

with the values

\[ \rho = \frac{2z}{na}\rho = \lambda r, \quad a = \frac{(4\pi e^2)}{\mu v^2} \]

and here, if we take into account hydrogen atom \((z=1)\) then, \( a = 1 \) for the radius of the first Bohr orbit [23].

Fourier Transform of Normalized HTOs

We use the symmetric version of the Fourier transform, namely, a given function \( f(\vec{r}) \) and its Fourier transform \( F(\vec{p}) \) are connected by the relationships

\[ F(\vec{p}) = (2\pi)^{-3/2} \int e^{-i\vec{p} \cdot \vec{r}} f(\vec{r}) d^3r \] (4)

\[ f(\vec{r}) = (2\pi)^{-3/2} \int e^{i\vec{p} \cdot \vec{r}} F(\vec{p}) d^3p \] (5)

Now, let’s obtain the Fourier transform of normalized HTOs. In momentum space, general expression of Fourier transform of normalized HTOs is

\[ U_{nl}^m(\vec{p}) = (2\pi)^{-3/2} \int e^{-i\vec{p} \cdot \vec{r}} \psi_{nl}^m(\vec{r}) d^3r \] (6)

Later, with help of Eq (3) and the following Rayleigh expansion [24]

\[ e^{2i\vec{k} \cdot \vec{r}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} (-i)^l j_l(x) \left[ \left( Y_l^m(\theta_1, \phi_1) \right)^* \left( Y_l^m(\theta_2, \phi_2) \right) \right] \] (7)

and also by taking value \( \rho = \lambda r \), we can write

\[ U_{nl}^m(\vec{p}) = -\left(2\pi\right)^{-3/2} \sum_{k=0}^{\infty} \sum_{m=-k}^{k} (-i)^k Y_k^m(\vec{p} \cdot \vec{r}) \left( \frac{n-l-1!}{2n[(n+l)!]} \right)^{1/2} \]
If we consider the orthogonality of real spherical harmonics in case of $k = l$ and $m' = m$, then, value of angular integral in Eq. (8) happens 1 and two sums over $k$ and $m'$ remove. Later, if the $j_k(pr)$ has been taken into the account, and by spherical Bessel functions in Ref. [25], finally, Eq. (8) can be rewritten as

$$U_{nl}^m(\bar{p}) = -p^{-1/2}(-i)^l Y_l^m(\bar{p}/p) \left\{ \left( \frac{\lambda}{2n[(n+l)!]^2} \right)^{1/2} \sum_{\alpha=0}^{n} \sum_{\beta=0}^{l} \left( \frac{1}{\nu!} \right) \Gamma(c + \alpha, -\nu \nu \lambda) \right\}$$

where, $J_l(pr)$ is Bessel function. To calculate this integral easily, we need to use explicit configurations of generalized Laguerre polynomials are presented below separately [26]

$$L_\beta^\alpha(\lambda r) = \sum_{z=0}^{\beta} \left( \frac{\beta + \alpha}{z} \right) \lambda^z (1-\lambda)^{\beta-z} L_\beta^\alpha(r)$$

$$L_\beta^\alpha(r) = \sum_{\nu=0}^{\beta} \left( \frac{\beta + \alpha}{\beta - \nu} \right) \frac{(-r)^\nu}{\nu!}$$

after some analytical treatments, Eq. (9) can be rewritten with radial integral as

$$U_{nl}^m(\bar{p}) = -p^{-1/2}(-i)^l Y_l^m(\bar{p}/p) \left\{ \left( \frac{\lambda}{2n[(n+l)!]^2} \right)^{1/2} \sum_{\alpha=0}^{n} \sum_{\beta=0}^{l} \left( \frac{1}{\nu!} \right) \Gamma(c + \alpha, -\nu \nu \lambda) \right\}$$

Analytical Results and Discussion

Integral form in the Eq. (12) consist three functions and its solution is quite difficult, for the solution of this integral, we will use the following relations separately [25]

$$\int_0^\infty e^{-r} J_{l+1/2}(pr) r^{l+1/2} dr = \frac{1}{\sqrt{\pi}} \binom{k-l}{2} \left( \frac{2p}{\alpha} \right)^{(k+l)/2} C_{k+l}^l \left( \frac{\alpha}{\sqrt{\alpha^2 + p^2}} \right)$$

$$\int_0^\infty e^{-ar} J_l(pr) r^{m-1} dr = \frac{\left( \frac{p}{2\alpha} \right)^\nu \Gamma(v+\mu)}{\alpha^\mu \Gamma(v+1)} _2F_1 \left( \frac{v+\mu}{2}, \frac{v+\mu+1}{2}; v+1; -\frac{p^2}{\alpha^2} \right)$$
First, if we use integral form of Eq. (13) into the Eq. (12) with the consideration of regular solid harmonics in Eq. (2), and then, the Fourier transform of normalized HTOs is obtained in terms of Gegenbauer polynomials by

\[
U_{n\ell}^m(\vec{p}) = \left\{ \frac{(n-l-1)!}{2n[(n+l)!]} \right\}^{1/2} \sum_{z=0}^{n+l-z} \sum_{\nu=0}^{n+l-z} \left( \frac{n+3l+1}{z} \right) \left( \frac{n+3l-z+1}{n+l-z-\nu} \right) \frac{(-1)^{\nu+1}}{\nu!} \lambda^{n+2l-2z+3/2} (1-\lambda)^{z-\nu} \\
\hspace{2cm} \frac{2^{l+1/2}l!(\nu+1)!}{\sqrt{\pi} \Gamma((\lambda/2)^2+p^2)} C^{\nu+1}_{\nu+1} \left( \frac{\lambda/2}{\sqrt{((\lambda/2)^2+p^2)}} \right) S^{n}_{\ell}(i\vec{p})
\]

(15)

In the same way, by using integral form in Eq. (14), the Fourier transform of normalized HTOs is found by hypergeometric functions as follow

\[
U_{n\ell}^m(\vec{p}) = \left\{ \frac{(n-l-1)!}{2n[(n+l)!]} \right\}^{1/2} \sum_{z=0}^{n+l-z} \sum_{\nu=0}^{n+l-z} \left( \frac{n+3l+1}{z} \right) \left( \frac{n+3l-z+1}{n+l-z-\nu} \right) \frac{(-1)^{\nu+1}}{\nu!} \lambda^{n-2\nu-3/2} (1-\lambda)^{z} \\
\hspace{2cm} \frac{2^{l+1/2}l!(\nu+1)!}{\Gamma((l+3/2)^2)} \frac{\Gamma(2l+\nu+3)}{\Gamma(l+3/2)} \frac{2l+\nu+3}{2}, \frac{2l+\nu+4}{2}, l+3/2; -\frac{p^2}{(\lambda/2)^2} \right\} S^{n}_{\ell}(i\vec{p})
\]

(16)

Our analytical results can be compared with their functional contents. If equations (15) and (16) are taken into consideration, in these equations, angular parts \( S^{n}_{\ell}(i\vec{p}) \) regular solid harmonics are the same. But, their radial parts have different functional characteristics. Fourier transform of normalized HTOs in equation (15) has been obtained in terms of Gegenbauer polynomials, besides, equation (16) by hypergeometric functions. These two equations are denoted in momentum space. Even if radial part of Eqs. (15) and (16) are different functions, it can be seen from Table 1 that their calculated numerical results are completely same. This proves that new obtained relations for Fourier transform of normalized HTOs produce exactly the same numerical results. Table 1 has been established for the values of \( \lambda = 2 \) (\( \lambda = 2z/na_\mu \) and for hydrogen atom \( z = 1 \), \( n = 1 \), \( a_\mu = 1 \)) and quantum numbers \( n \), \( l \). In Table 1, \( p \) is magnitude of momentum space vector \( \vec{p} \) and we prefer to use value of \( n \) until 15 because of numerical results decrease rapidly for larger values.

### Table 1. Comparison of numerical results for radial part of Fourier transform of normalized HTOs.

<table>
<thead>
<tr>
<th>( n )</th>
<th>( l )</th>
<th>( p )</th>
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<tr>
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In reality, behaviors of graph of Gegenbauer polynomials and hypergeometric functions are not analogous graphs. But, if we consider Figure 1, radial functions in Eqs. (15) and (16) produces same graphs even if they contain Gegenbauer polynomials and hypergeometric functions. Figure 1 shows that graph of radial parts of Fourier transform of HTOs exponentially decrease. Namely, Fourier transform of HTOs are also one type of the other ETOs. So, we can easily say that our new analytical and computational results are accurate and compatible. In Table 1 and Figure 1, atomic units are used for all values of quantum mechanical parameters. Numerical results and graph in this study are obtained by using the Mathematica programming language [27].

![Figure 1. Graph of radial part of Fourier transform of normalized HTOs (FT of HTOs) versus $p$ for quantum numbers $n = 3$, $l = 2$, and atomic parameter $2\lambda$. This graph can be plotted by using Eq. (15) or (16).](image)

In this paper we analyzed mathematical and quantum mechanical properties of normalized HTOs and their Fourier transforms. After these operations, we produce new and useful mathematical findings for them, and we believe that they will contribute to the development of the other atomic ETOs. So, we would like to say that obtained analytical results in this paper can be a good step for the future molecular integral calculations and mathematical applications.

References