



The hydrogen atom in the momentum representation; a critique of the variables comprising the momentum representation

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ABSTRACT

We examine critically the solutions for the hydrogen atom in momentum space. We demonstrate that the approach by Podolsky and Pauling (Physical Review 1928, 34, 109) to such a transformation was inconsistent with Podolsky's preceding analysis (Physical Review 1928, 32, 812) and yields functions that fail to utilize quantum-mechanically acceptable variables in momentum space. This practice arose from the commonplace belief that functions in momentum space are Fourier transforms of those in position space. We show that proper quantum-mechanical functions are obtainable through presentation of a clear definition of momentum space based on DeWitt's transformation (Physical Review 1952, 85, 653). This method allows us to obtain proper wave functions for the hydrogen atom in momentum space.

1. Introduction

In this article we aim to examine *the other half* of wave mechanics. The establishment of a wave function, which contains all information about a system consistent with the uncertainty principle, is one goal of quantum theory. This wave function is generally obtained on solving the Schroedinger equation in terms of position variables in space of n dimensions; n is the number of degrees of freedom available to the system. This space is termed position space or the position representation. There is, however, an alternative representation, which is most readily understood in terms of the commutation relations between the position variables (q_n) and the corresponding momentum variables (p_n). The fact that these variables are conjugate to each other implies an equivalence between the wave function of the system in terms of the position variables and that in terms of the momentum variables. Wave functions in the latter space, the momentum space or momentum representation, also contain all information about a system consistent with the uncertainty principle, but this momentum space has been, by and large, neglected. The reasons for this practice are varied, but one glaring reason is that a proper definition of momentum space is lacking. Many scientists state that the connection between momentum space and position space is expressed in terms of a Fourier transform. Except in the case of Cartesian coordinates, this statement is incorrect; this misunderstanding has led many scientists in the wrong direction, and has led to many inconsistencies. Our intention here is to explore some inconsistencies and to develop a definition of momentum space that is

quantum-mechanically consistent, so as to enable an establishment of procedures to solve the Schroedinger equation in momentum space. We then apply these ideas directly to a solution of the hydrogen atom in momentum space. Some advantages and disadvantages of exploring this half of wave mechanics are also examined.

The foundations of quantum mechanics were established nearly a century ago. The amplitude functions, which are algebraic solutions of the time-independent Schroedinger equation, are expressed explicitly in terms of either spatial coordinates or momentum variables. These solutions in position space were originally obtained for several simple but important systems such as the harmonic oscillator (see Appendix A) and the hydrogen atom (see below and Appendix B); these results laid the foundation for the extension of wave mechanics and provided a basis of our current knowledge and treatment of atomic and molecular structure. Much of that work involved obtaining valid functions that are solutions to the differential equation and the matrix formulations of the quantum theory. The fact that the momentum representation is totally equivalent to the position representation should presage considerable attention to the momentum functions, for the possibility that they could provide some advantage over functions in position space for various problems. This promise has not, however, been realised. We contend that part of the reason for this imbalance lies in the difficulties in establishing the proper momentum variables as analogues of the position coordinates. These difficulties stem from various misconceptions about the nature of the relations between the two representations, and the transformations used to generate them. For the particular case of the

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hydrogen atom, we investigate these difficulties in this article.

We first trace the development of the choice and use of variables used in determining the momentum analogues of the variables in position space. We explore the difficulties encountered and the misunderstandings that caused these problems. We then present a proper definition of the momentum representation, and illustrate its application to the foundational problem of the hydrogen, or one-electron, atom.

2. Conjugate variables in multiple dimensions

In the particular case of a system involving only one spatial dimension, the displacement q and momentum p/\hbar are directly conjugate variables. For a system in three spatial dimensions other than for Cartesian coordinates, a problem of the conjugacy of variables arises. Because the commutator between displacement q and momentum p in one spatial dimension in assumed Cartesian coordinates, i.e. $[p, q] = pq - qp$, evaluates not to zero but to $i\hbar$, products such as p^2 and $q^{-1}p$ are inequivalent. For variables (q_1, q_2, \dots, q_n) in position space in any set of n dimensions, the volume element is $dV = g(q_1, q_2, \dots, q_n) dq_1 dq_2 \dots dq_n$, in which $g(q_1, q_2, \dots, q_n)$ is the Jacobian of the transformation between variables in the two sets. To each variable (q_1, q_2, \dots, q_n) in position space there is a corresponding variable (p_1, p_2, \dots, p_n) in momentum space such that each momentum variable is chosen conjugate to a corresponding position space variable: $[p_k, q_k] = i\hbar$.

In 1928, Podolsky [1] derived the quantum-mechanically correct form of the Hamiltonian for conservative systems. In that work, he began with the Schrodinger equation in Cartesian coordinates, and converted it to spherical polar coordinates. He then utilized the transformation that, for each momentum variable p_k ($=p_r, \theta_p, \phi_p$), there exists an expression $p_k = -i\hbar (\partial/\partial q_k)$. He showed that, with such a transformation, an equation is obtained that differs from the correct Hamiltonian, and that hence cannot truly represent the momentum equation. To overcome this impediment, he introduced an arbitrary n -dimensional coordinate transformation such that the element of length is

$$ds^2 = \sum_{r=1}^n \sum_{s=1}^n g_{rs} du_r du_s \tag{1}$$

in which $g_{rs} = g_{sr}$ are elements of the Jacobean of transformation g . He introduced also the notation $g^{rs} = (\text{minor of } g_{rs})/g$. Letting V be the potential energy, he then obtained the quantum-mechanically correct form of the Hamiltonian as

$$H = \frac{1}{2\mu} \sum_{r=1}^n \sum_{s=1}^n g^{-1/4} p_r g^{1/2} g^{rs} p_s g^{-1/4} + V \tag{2}$$

This formulation preserves the presumption that $p_k = -i\hbar (\partial/\partial q_k)$. When the representation for the position space is in Cartesian coordinates, $g = 1$, as for the harmonic oscillator presented in Appendix A.

3. Derivation of Podolsky and Pauling for the one-electron atom

In 1929, Podolsky and Pauling [2] derived what they claimed to be a momentum distribution for hydrogen-like atoms. They abandoned Podolsky's promising approach of adopting a quantum-mechanically correct Hamiltonian in favor of the utilization of a method resembling a Fourier transform. They chose a momentum coordinate system (p_r, θ_p, ϕ_p) in which p_r represents the magnitude of the total momentum as $p_r = (p_x^2 + p_y^2 + p_z^2)^{1/2}$; θ_p and ϕ_p denote angles that specify the orientation of the momentum vector relative to the Cartesian coordinate axes. They then obtained momentum eigenfunctions by means of a transformation of amplitude functions in position space to a momentum space consisting of variables (p_r, θ_p, ϕ_p) . The resulting functions became products of spherical harmonics of (θ_p, ϕ_p) , i.e. $Y_m^l(\theta_p, \phi_p) = P_m^l(\theta_p) e^{im\phi_p}$, with

Gegenbauer polynomials $C_r^v(p_r)$ in the radial component. In the detailed description that follows, we apply a consistent notation, even though somewhat different from that of the original authors.

In three spatial dimensions, the Fourier transform of amplitude function $\Psi_{n,l,m}(x, y, z)$ in Cartesian coordinates to a corresponding amplitude function in momentum variable p with components (p_x, p_y, p_z) is

$$\chi_{n,l,m}(p_x, p_y, p_z) = \frac{1}{h^{3/2}} \int_{-\infty}^{+\infty} \Psi_{n,l,m}(x, y, z) e^{\left(\frac{-2i\pi(xp_x + yp_y + zp_z)}{h}\right)} dx dy dz \tag{3}$$

Podolsky and Pauling [2] applied standard relations between Cartesian and spherical polar coordinates,

$$x = r \sin(\theta) \cos(\varphi), y = r \sin(\theta) \sin(\varphi), z = r \cos(\theta) \tag{4}$$

and assumed the analogous relations, despite Podolsky's previous recognition of the necessity of conjugate relations between the coordinate and momentum variables [1]. Instead they chose for the components of linear momentum:

$$p_x = p_r \sin(\theta_p) \cos(\varphi_p), p_y = p_r \sin(\theta_p) \sin(\varphi_p), p_z = p_r \cos(\theta_p) \tag{5}$$

According to this equation for the transformation between coordinate space with $\Psi_{n,l,m}(r, \theta, \phi) = R_{n,l}(r) Y_{l,m}(\theta, \phi)$ and momentum space,

$$\begin{aligned} \chi_{n,l,m}(p_r, \theta_p, \varphi_p) &= \frac{1}{h^{3/2}} \int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{n,l,m}(r, \theta, \varphi) e^{\left(\frac{-2i\pi(\sin(\theta) \sin(\theta_p) \cos(\varphi_p - \varphi) + \cos(\theta) \cos(\theta_p)) r p_r}{h}\right)} r^2 \\ &\quad \sin(\theta) d\varphi d\theta dr \end{aligned} \tag{6}$$

Podolsky and Pauling proceeded to generate an expression for amplitude functions in their presumed momentum space of an atom of atomic number Z with one electron of this form,

$$\begin{aligned} \chi_{n,l,m}(p_r, \theta_p, \varphi_p) &= -2e^{im\varphi_p} \sqrt{\frac{2(2l+1)(l-m)!(n-l-1)!}{(l+m)!(n+l)!}} \\ &\quad \left[(-4in p_r)^l l! n^2 (Z p_0)^{\frac{5}{2} + l} P(l, m, \cos\theta_p) C \left(n-l \right. \right. \\ &\quad \left. \left. -1, l+1, \frac{-Z^2 p_0^2 + n^2 p_r^2}{Z^2 p_0^2 + n^2 p_r^2} \right) \frac{1}{\pi} \left(\frac{1}{(Z^2 p_0^2 + n^2 p_r^2)} \right)^{l+2} \right] \end{aligned} \tag{7}$$

in which appear associated Legendre functions $P(l, |m|, \cos(\theta_p))$ of the first kind and Gegenbauer [or ultraspherical functions $C(n-l-1, l+1, \dots)$. The atomic unit of momentum denoted p_0 is defined as $p_0 = \hbar/a_0$ in terms of Bohr radius a_0 . For all allowed values of quantum numbers n for energy and l and m for angular momentum, and for atomic number Z , this amplitude function is fully normalized according to this integral:

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \chi_{n,l,m}(p_r, \theta_p, \varphi_p)^* \chi_{n,l,m}(p_r, \theta_p, \varphi_p) p_r^2 \sin(\theta_p) d\theta_p d\varphi_p dp_r = 1 \tag{8}$$

With this amplitude function Podolsky and Pauling calculated both the probability of an electron having momentum between p_r and $p_r + dp_r$ and the expectation value $\langle p_r^2 \rangle$; as these quantities have no angular dependence, there is no test of the angular dependence of their momentum function involving θ_p and ϕ_p . The expectation value of momentum squared, valid for all values of l, m :

$$\langle p_r^2 \rangle = Z^2 p_0^2 / n^2 \tag{9}$$

agrees with the corresponding result in coordinate space. A textbook by Bransden and Joachain [3] presents a similar derivation of the radial dependence of the amplitude function, again yielding Gegenbauer polynomials, but ignores the angular dependence.

Hylleraas [4] solved a differential equation to obtain similar results. He recognized that radial variable r in position space is expressed as a differential operator in momentum space, assumed to be $i\hbar d/dp_r$,

$$\left[(p_r^2 - 2mE)^2 \left[\frac{d^2}{dp_r^2} + \frac{2d}{p_r dp_r} - \frac{\ell(\ell+1)}{p_r^2} \right] + (p_r^2 - 2mE) \left[2p_r \frac{d}{dp_r} + 2 \right] + 8mRh \right] \chi = 0 \quad (10)$$

containing electronic mass m , energy E and Rydberg constant R . With the appropriate substitution

$$p_r = \sqrt{\frac{2mE(1+\zeta)}{1-\zeta}} \quad (11)$$

the resulting equation had solutions of Gegenbauer polynomials $C_{n-\ell-1}^{\ell+1}(\zeta)$, the same as obtained by Podolsky and Pauling. Hylleraas converted those Gegenbauer polynomials to Legendre functions so as to generate a product of Legendre functions of two variables. The equations for θ_p and ϕ_p were treated in the same manner. The final result, not normalized, is expressible as

$$\chi_{n,l,m}(p_r, \theta_p, \varphi_p) = \frac{p_r p_0^3 P\left(n + \frac{1}{2}, l + \frac{1}{2}, \frac{n^2 p_r^2 - p_0^2}{n^2 p_r^2 + p_0^2}\right) P(l, m, \theta_p) e^{im\phi_p}}{\left(\frac{n^2 p_r^2 + p_0^2}{p_0^2}\right)^l (n^2 p_r^2 + p_0^2)^2} \quad (12)$$

In contrast, Fock [5] adopted an integral-equation approach for the eigenfunctions of the total momentum variable (p_r). He recognized that, if r had an analogue $-i\hbar d/dp_r$ in momentum space, the inverse operator ($1/r$) associated with the Coulombic potential energy should be expressed as an integral operator. This treatment led to the integral equation

$$p_r \chi(p_r) - \frac{mZe^2}{\pi^2 \hbar} \int \frac{\chi(p_r^*) dp_r^*}{|p_r - p_r^*|^2} = 2mE\chi(p_r) \quad (13)$$

for the solution of which he resorted to a four-dimensional hyper-spherical polar-coordinate scheme. He then obtained:

$$\chi_{n,l,m}(\alpha, \theta, \phi) = \Pi_l(n, \alpha) Y_{l,m}(\theta, \phi) \quad (14)$$

Therein angles α, θ, ϕ are spherical coordinates of a point on a hypersphere, but at the same time angles θ and ϕ are ordinary spherical coordinates characterizing the momentum direction. On projection back to three-dimensional space, he apparently recovered the results of Hylleraas. The radial function $\Pi_l(n, \alpha)$ that appears as a product with the spherical harmonics, $Y_{l,m}(\theta, \phi)$, as in preceding work, was not elaborated explicitly.

4. Deficiencies of the derivation by Podolsky and Pauling

The above approach presents several important difficulties. We note first that variable p_r represents the magnitude of the total momentum, and is not chosen conjugate to any variable in position space; no valid commutation relation is given for p_r . Uncertainty relations with a corresponding coordinate in position space are not presented. Although p_r has units of momentum, and represents a measurable quantity, it represents no proper quantum-mechanical variable that can serve as a foundation of a true momentum representation; the reason is that operator $p_r = -i\hbar \partial/\partial r$ is not Hermitian [6]. The supposition that momentum space consists of functions that are the Fourier transform of a set of variables (q_1, q_2, \dots, q_n) in coordinate space implies a definition of the momentum representation as (p_1, p_2, \dots, p_n) in which $p_k = -i\hbar \partial/\partial q_k$ for every k . Dirac showed that, for example, with spherical polar coordinates this definition leads to a recognition that p_r is not real [7]. To find an expression that is real, the canonical coordinate must be written as $p_r = -i\hbar (\partial/\partial q_r - 1/r)$. The correct momentum space can thus not

be connected to position space, in other than Cartesian coordinates, with a simple Fourier transform.

The angular-momentum variables (θ_p, ϕ_p) present additional difficulties; they were defined in terms of ‘‘spatial polar coordinates of the total momentum vector referred to the same axes as the coordinates (r, θ, ϕ) of the electron’’ [2]. These variables should hence be regarded as properties of position space, rather than being termed variables in momentum space; they are defined as the angles connecting the radial momentum vector p_r to the Cartesian *spatial* axes (x, y, z). No commutation relations between the momentum variables (θ_p, ϕ_p) and the corresponding position variables (θ, ϕ) were presented, nor were valid uncertainty relations derived. Furthermore, one can readily show that the Fourier transform of the function $e^{im\phi p}$ is a Dirac δ -function, *not* $e^{im\phi p}$ as given by Podolsky and Pauling. Similarly, the Fourier transform of associated Legendre polynomials can be shown to be Bessel functions to various integer and half-integer orders, *not* associated Legendre polynomials of $\cos\theta_p$ as given by Podolsky and Pauling. The procedure of Podolsky and Pauling leads to the conclusion that, for the angular parts, the wave functions in momentum space have a form identical with that in wave functions in coordinate space. The only Hamiltonian for which the wave functions in position and momentum space have identical forms is that of the harmonic oscillator [See Appendix A]. The inevitable conclusion is that, despite their claim, Podolsky and Pauling failed to derive quantum-mechanically acceptable eigenfunctions for the hydrogen atom in the momentum representation. Hylleraas and Fock, separately, adopted the angular parts of position space for their variables in momentum space, and likewise failed to derive their sought eigenfunctions in a form that is quantum-mechanically acceptable.

5. Definition of momentum space

In Cartesian space, variables p, q range from $[-\infty, \infty]$. For a single particle in one dimension, the Hamiltonian is typically written as

$$H(p, q) = p^2/2m + V(q) \quad (15)$$

in which μ is the mass of the particle and $V(q)$ is the potential-energy function. To convert this classical Hamiltonian function to a quantum-mechanical operator, we express the momentum as an operator,

$$p \rightarrow -i\hbar d/dq \quad (16)$$

We seek solutions of the resulting differential equation for the eigenvalues represented by E :

$$H\psi(q) = E\psi(q) \quad (17)$$

$\Psi(q)$ are the eigen functions, expressed as functions of the position of the particle. One can easily show that a commutation expression between the conjugate operators can be written

$$[p, q] = i\hbar \quad (18)$$

leading to an uncertainty relation of the form,

$$\Delta p \Delta q \geq 1/2\hbar \quad (19)$$

The transformed functions in momentum space are connected to the functions in position space through the transform:

$$\chi(p) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} S(p, q) \psi(q) dq \quad (20)$$

Textbooks on quantum mechanics commonly state that this transform is the Fourier transform [8] as exemplified for the harmonic oscillator (Appendix A), in which case we can write simply

$$S(p, q) = e^{-(i/\hbar)qp} \quad (21)$$

As pointed out above, this relation is correct only for Cartesian coordinates. For curvilinear coordinates, one must choose a transform that preserves the proper conjugate relations between variables in

momentum space and those in position space. The general form that DeWitt [9] obtained holds for all transformations between a Cartesian space (x_1, x_2, \dots, x_n) in n dimensions and an arbitrary coordinate system (q_1, q_2, \dots, q_n) such that volume element $dV = dx_1 dx_2 \dots dx_n$ is transformed into $dV = g dq_1 dq_2 \dots dq_n$; here g is the Jacobian of the transformation [10]. Under these circumstances, the most general transform between amplitude functions $\psi(q_1 \dots q_n)$ in position space and amplitude functions $\chi(p_1 \dots p_n)$ in momentum space is

$$\chi(p_1 \dots p_n) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} S(p_1 \dots p_n, q_1 \dots q_n) \psi(q_1 \dots q_n) g dq_1 \dots dq_n \quad (22)$$

in which

$$S(p_1 \dots p_n, q_1 \dots q_n) = \frac{1}{\sqrt{g}} e^{-i(i/\hbar)q \cdot p} \quad (23)$$

We take as the definition of n -dimensional momentum space that set of n momentum variables (p_1, p_2, \dots, p_n) , each chosen properly conjugate to the corresponding variables (q_1, q_2, \dots, q_n) in position space. Due to DeWitt's contributions to our understanding of this transformation, we suggest calling this the DeWitt transformation. The correct Hermitian form of each momentum space variable is then

$$p_k \rightarrow -i\hbar \left(\frac{\partial}{\partial q_k} + \frac{1}{2g} \frac{\partial g}{\partial q_k} \right) \quad (24)$$

6. The function for the hydrogen atom in momentum space

We proceed to develop an amplitude function for the hydrogen atom in the momentum representation based on DeWitt's formulation of momentum variables in spherical polar coordinates [8]. We consider three momentum variables (p_r, θ_p, ϕ_p) , which must be chosen as conjugates to the corresponding position variables (r, θ, ϕ) [11]. As the hydrogen atom is separable in the position representation, we transform separately the radial equation for $R(r)$ and the angular equations for $\Theta(\theta)$ and $\Phi(\phi)$. In this product for the momentum functions

$$\chi(p_r, \theta_p, \phi_p) = \alpha(p_r) \beta(\theta_p) \rho(\phi_p) \quad (25)$$

the eigenfunctions in the momentum representation corresponding to $R(r)$ are called); the eigenfunctions in the momentum representation corresponding to $\Theta(\theta)$ and $\Phi(\phi)$ become $\beta(\theta_p)$ and $\rho(\phi_p)$, respectively. Recalling that the eigenfunctions of angular momentum operators L^2 and L_z in position space are spherical harmonics, $Y_{l,m}(\theta, \phi)$, with eigenvalues $l(l+1)$ and m , respectively, the corresponding eigenfunctions in the momentum representation must satisfy these expressions:

$$L^2 \beta(\theta_p) \rho(\phi_p) = l(l+1) \hbar^2 \beta(\theta_p) \rho(\phi_p) \quad (26)$$

$$L_z \rho(\phi_p) = m \hbar \rho(\phi_p) \quad (27)$$

We examine first momentum space variable p_r , which is conjugate to position space radial variable r . The value of g for the transformation from $R(r)$ to $\alpha(p_r)$ is r^2 . As suggested in Eq. (24) above, we obtain the real conjugate momentum variable to be expressed as [7]

$$p_r \rightarrow -i\hbar ((\partial/\partial r) + 1/r) \quad (28)$$

The corresponding expressions for the position space variables are

$$r \rightarrow -i\hbar r^{-1} \rightarrow (i/\hbar) \int_{-\infty}^r f(p'_r) dp'_r \equiv \text{I} \quad (29)$$

In the latter expression for r^{-1} the path of integration is along the real axis from $-\infty$ to p_r . The radial part of the Hamiltonian is written in position space as

$$H = \frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{\ell(\ell+1)}{r^2} \right) - \frac{Ze^2}{4\pi\epsilon_0 r} \quad (30)$$

in which l is the quantum number for total angular momentum, obtained from the solution of the angular problem. With the radial

eigenfunction in momentum space as $\alpha(p_r)$, we write

$$H\alpha(p_r) = E\alpha(p_r) \quad (31)$$

On substituting, we obtain the following integral equation for the momentum representation:

$$(p_r^2 - 2\mu E + l(l+1)\mathbf{I}^2 + 2\mu Ze^2 \mathbf{I})\alpha(p_r) = 0 \quad (32)$$

This second-order integral equation in p_r is readily solved for $\alpha(p_r)$ with standard techniques [12]. On taking the second derivative of equation (32) to eliminate the integral operators and solving the resulting rather simple differential equation (see Eqs. (11)–(15) of Ref. [11]), this procedure yields this general result for all n and l .

$$\alpha_{n,l}(p_r) = N_{n,l} \sum_{k=0}^{n-l-1} \frac{(n-l-1)! 2^k (l+k+1)!}{k! (n-l-k-1)! (2l+k+1)!} \left(\frac{ip_0}{n} \right)^{(l+k+2)}$$

$$N_{n,l} = \frac{2^{l+1} \frac{\pi}{\sqrt{p_0}}}{(n-l-1)! \sqrt{\pi} \sum_{k=0}^{n-l-1} \frac{\sum_{j=0}^{n-l-1} \frac{(-1)^{(k+j)} (2l+k+j+2)!}{j! (n-l-j-1)! (2l+j+1)!}}{k! (n-l-k-1)! (2l+k+1)!}} \quad (33)$$

This function $\alpha_{n,l}(p_r)$ is fully normalised for all n, l such that:

$$\int_{-\infty}^{\infty} \alpha_{n,l}(p_r) \alpha_{n,l}^*(p_r) dp_r = 1 \quad (34)$$

This function $\alpha_{n,l}(p_r)$ is also generated directly with this quasi-Fourier or DeWitt transform,

$$\alpha_{n,l}(p_r) = \int_0^{\infty} R(r) e^{ip_r r} r dr \quad (35)$$

in which factor r in the integrand results from the appropriate Jacobean of the transformation. In the interest of space, we present in Appendix B the solution to the parts of the momentum functions corresponding to the angular parts in coordinate space. In brief, the functions $\beta_{l,m}(\theta_p)$ are found to be sums of Bessel functions of half-integer order; the function $\rho(\phi_p)$ is represented as a complex exponential function.

Although these functions $\alpha_{n,l}(p_r)$ and $\beta_{l,m}(\theta_p)$ seem complicated, we present a few amplitude functions $\chi_{n,l,m}(p_r, \theta_p, \phi_p)$ for hydrogen in the momentum representation to illustrate the simplicity of these results, recalling that the total functions are products as defined in Eq. (27). For $n = 1$ and 2 we obtain these expressions, which are fully normalised.

$$\chi_{1,0,0}(p_r, \theta_p, \phi_p) = \frac{\left(\frac{1-l}{2}\right) \sqrt{2p_0^3} \sin(\theta_p) (e^{2i\pi\phi_p} - 1)}{\epsilon_p \pi^2 (ip_0 - p_r)^2 \phi_p}$$

$$\chi_{2,0,0}(p_r, \theta_p, \phi_p) = \frac{(1-i) \sqrt{p_0^3} (ip_0 + 2p_r) \sin(\theta_p) (e^{2i\pi\phi_p} - 1)}{\epsilon_p \pi^2 (ip_0 - 2p_r)^2 \phi_p}$$

$$\chi_{2,1,0}(p_r, \theta_p, \phi_p) = \frac{(-2+2i) \sqrt{p_0^5} (\epsilon_p \cos(\theta_p) - \sin(\theta_p)) (e^{2i\pi\phi_p} - 1)}{\epsilon_p \pi^2 (ip_0 - 2p_r)^2 \phi_p}$$

$$\chi_{2,1,1}(p_r, \theta_p, \phi_p) = -\frac{(1+i) \sqrt{2p_0^5} J(1, \epsilon_p) (e^{2i\pi(\phi_p+1)} - 1)}{2\pi \epsilon_p (ip_0 - 2p_r)^2 (1 + \phi_p)} \quad (36)$$

Expectation values of observable quantities are readily calculated with these amplitude functions. For instance, for functions $\alpha_{n,l}(p_r)$ with $l = 0$, the calculations yield $\langle p_r \rangle = 0$, $\langle p_r^2 \rangle = p_0^2/n^2$. Expectation values $\langle r^j \rangle$ calculated with $\alpha_{n,l}(p_r)$ reproduce exactly the corresponding values calculated with $R(r)$ in coordinate space.

7. Discussion

We present some graphical properties of the quantum-mechanically correct amplitude functions in momentum space. Fig. 1 presents the squares of the amplitude functions of p_r according to Eq. (33). In contrast to the radial eigenfunctions in space coordinates (r, θ, ϕ) , these functions become narrower as n increases. Whereas the radial functions (not shown) of Podolsky and Pauling [2] have $n - 1$ nodes along the momentum axis between $p_r = 0$ and ∞ at which the squared radial momentum equals zero, the functions of Lombardi [11] lack such

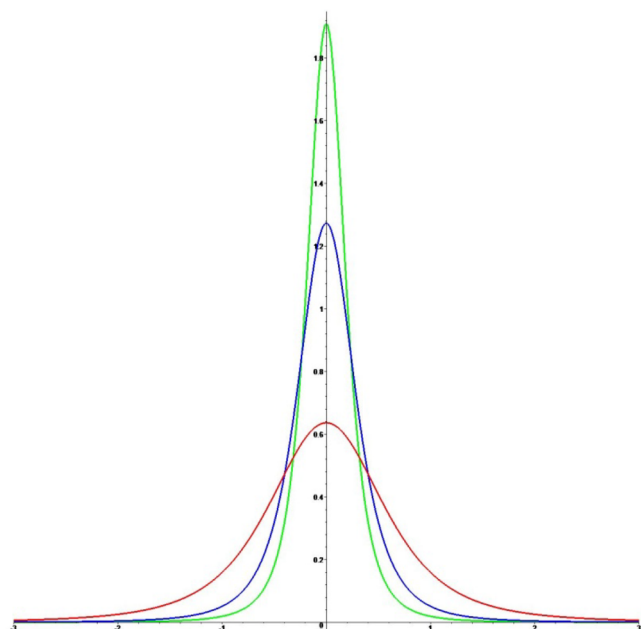


Fig. 1. Squared radial momentum $|\alpha_{n,0}(p_r)|^2$ as a function of p_r/p_0 from -3 to 3 for states with $n = 1$ (red), $n = 2$ (blue), $n = 3$ (green).

nodes. Both kinetic energy (relative to the centre of mass), which is proportional to the squared momentum, and potential energy vary continuously; their sum as the total energy of the hydrogen atom is subject to discrete values.

Fig. 2 shows the real parts of functions $\beta_{l,0}(\theta_p)$ for $l = 0, 1, 2$, which are oscillatory curves with amplitudes decaying as θ_p increases across its domain 0 to ∞ ; the corresponding curves for the imaginary parts are similar in each case. The squares of functions $\beta_{l,0}(\theta_p)$ show that the oscillations of these functions decay rapidly with increasing θ_p .

Fig. 3 shows the variation of $\rho_m(\phi_p)^2$ with ϕ_p for $m = -1, 0, 1$, which reveals the resemblance of these curves to the squares of sinc functions, of form $\sin(x)/x$.

Fig. 4 displays a surface of $|\chi_{1,0,0}(p_r, \theta_p, \phi_p)|^2 = |\alpha_{1,0}(p_r) \beta_{0,0}(\theta_p) \rho_0(\phi_p)|^2 = 0.001$ with p_r in unit p_0 . A sequence of figures resembling

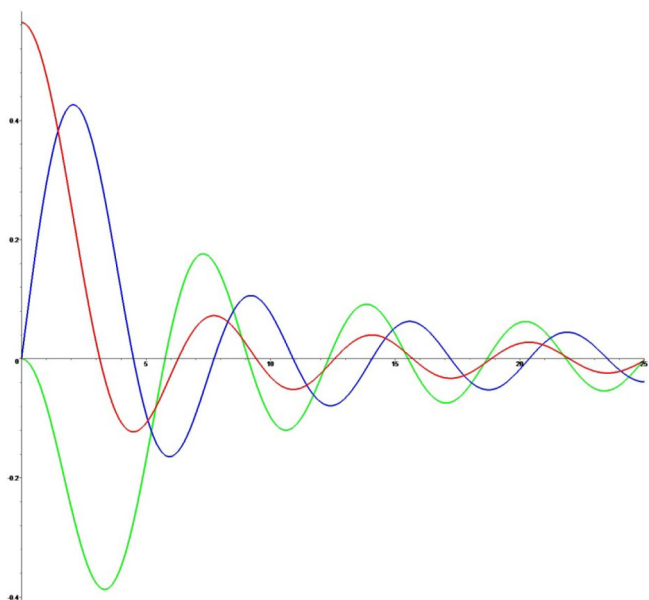


Fig. 2. Real parts of functions $\beta_{l,0}(\theta_p)$ for $l = 0$ (red), $l = 1$ (blue), $l = 2$ (green) vs θ_p from 0 to 25 .

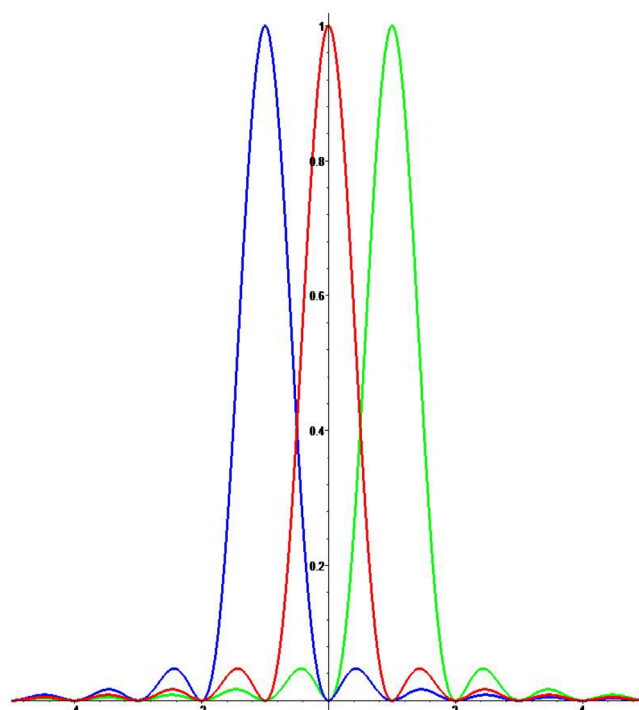


Fig. 3. Plots of $\rho_m(\phi_p)^2$ as a function of $-5 \leq \phi_p \leq 5$ for $m = 0$ (red), $m = 1$ (blue), $m = -1$ (green).

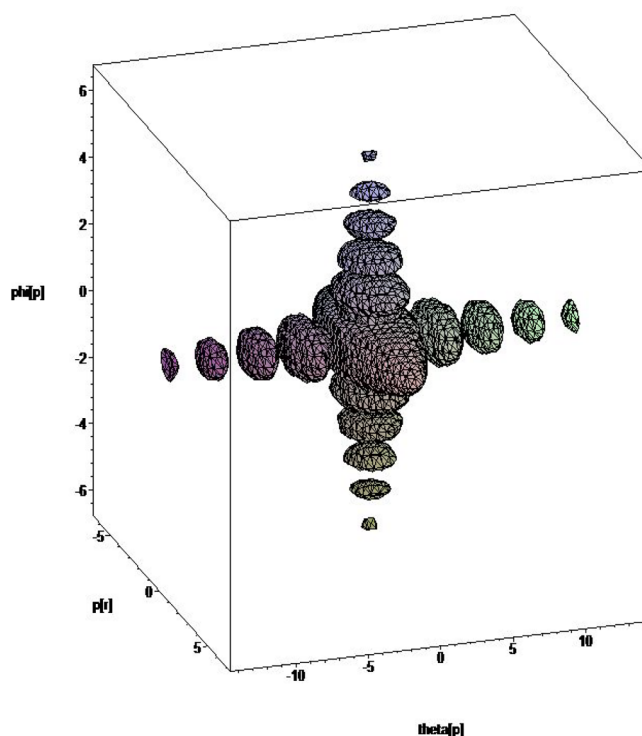


Fig. 4. Surface of $|\chi_{1,0,0}(p_r, \theta_p, \phi_p)|^2 = 0.001$ with p_r in unit p_0 .

prolate spheroids occurs along both axes θ_p and ϕ_p , with sizes gradually decreasing away from the origin; the major axis of each ellipsoid is parallel to axis p_r .

Fig. 5 shows an analogous surface of $|\chi_{2,1,0}(p_r, \theta_p, \phi_p)|^2 = 0.001$ with p_r in unit p_0 , which exhibits two columns of spheroids, one on either side of axis θ_p and parallel to that axis, and subsidiary spheroids gradually contracting in four other columns. Surfaces of $|\chi_{2,0,0}(p_r, \theta_p,$

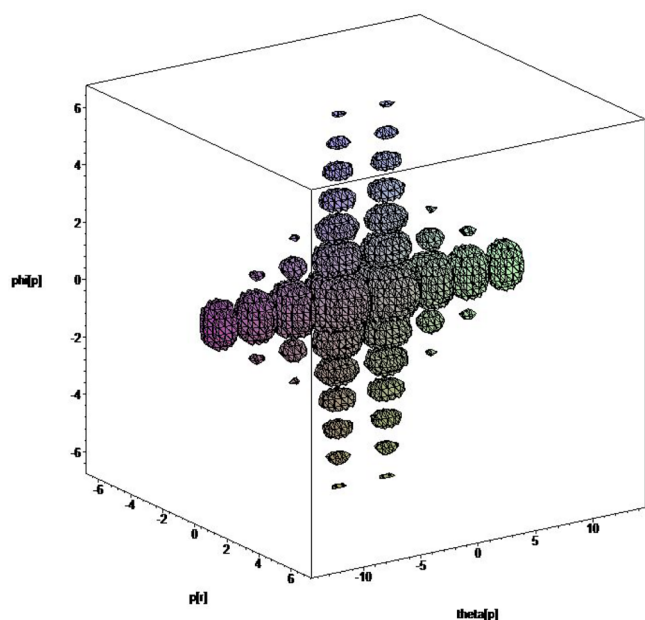


Fig. 5. Surface of $|\chi_{2,1,0}(p_r, \theta_p, \phi_p)|^2 = 0.001$ with p_r in unit p_0 ,

$|\chi_{2,1,1}(p_r, \theta_p, \phi_p)|^2$ resemble that of $|\chi_{1,0,0}(p_r, \theta_p, \phi_p)|^2$ except with additional small ellipsoids in subsidiary columns. This behaviour is expected on the basis of $\beta_{l,0}(\theta_p)$ in Fig. 2 and $\rho_m(\phi_p)$ in Fig. 3 that exhibit an oscillatory character. These shapes indicate that regions of momentum space in which the probability of the momentum function, indicated by its square, has a significant magnitude exist over appreciable ranges of θ_p and ϕ_p according to the oscillatory nature of both $\beta_{l,m}(\theta_p)$ and $\rho_m(\phi_p)$ as shown in Figs. 2 and 3.

8. Conclusion

A great mystery of this rather complicated history of the momentum-space formulation of the hydrogen atom is that Podolsky, in his 1928 paper [1], was on the verge of obtaining the correct solution. He derived a correct expression for the Hamiltonian (see Eq. (2)), and, with the proper definition of the momentum variables, could easily have solved the eigenvalue problem with simple differential or integral equations. Instead, discarding this promising approach, the very next year he collaborated with Pauling to attempt a direct transform of the solution in position space [2]; they did not even cite Podolsky's previous article [1]. No attempt was made to define the momentum-space variables in terms of the appropriate position variables, despite the fact that it was well known, for instance, from Weyl's work [13] cited by Podolsky and Pauling [2], that they should be related by appropriate commutation relations. Nor was any account taken of the required uncertainty relations between position and momentum. Although their results for the radial momentum function, expressed as sums of Gegenbauer functions, yielded a representation in terms of a momentum variable, the radial momentum variable was not chosen properly conjugate to position variable r . Regarding the angular variables, a long and rather convoluted derivation yielded eigenfunctions of which the forms were identical to those of the position eigenfunctions, despite the fact that the $\beta_{l,m}$ functions (see Appendix B, Eqs. (B9) and (B10)) are the quasi-Fourier transform of the associated Legendre polynomials. Nobody seemed to notice; both Hylleraas [4] and Fock [5] accepted these results uncritically. Even today, the functions of Podolsky and Pauling are taught in courses on quantum physics [3] as analogues in the momentum representation of the functions of the hydrogen atom in position space. It is also taught that momentum space functions are the Fourier transform of position space, which is true only for Cartesian coordinates.

In this article our purpose is to place our understanding of momentum space on a firm foundation. We call attention to the problems associated with the conventional approach of Podolsky and Pauling [2], and the misunderstandings that they have engendered. We point instead to an article by one of us [11] in which care was taken to ensure the proper choice of momentum-space variables for solutions to the differential and integral equations for the amplitude function of the hydrogen atom. We applied the formulation of DeWitt [9] to obtain a correct transformation of the functions. A transformation of amplitude functions from paraboloidal coordinates to the corresponding momentum representation [14] also conforms to DeWitt's formulation. The solutions for the hydrogen atom in position space form the basis for an understanding of much of atomic and molecular physics. As we demonstrate above, the resulting functions in momentum space have simple forms and are readily subject to derivatives and integrals, in calculations of expectation values or otherwise.

There are many problems in atomic and molecular physics that might benefit from an understanding of the correct functions in momentum space. There is a vast literature invoking various experimental techniques such as Compton scattering and (e, 2e) scattering [15,16]. The latter technique is a form of coincidence spectroscopy in which an electron collides with a target molecule or atom; the cross section for ionization is measured as a function of the momenta of the incident and two scattered electrons. Despite the difficulties with the momentum distribution obtained by Podolsky and Pauling, excellent fits have been obtained for the experimental results in hydrogen [17]. Satisfactory results have also been observed in noble gases [18]. One reason is that in their theory the angular functions are expressed in terms of variables in position space. As discussed in section 4 above, we treated this condition as disqualifying their claim to be a true momentum representation, but it appears useful for a purpose of comparison of the results with (e,2e) spectra with the same angular coordinates applied, enabling direct observation of the total momentum distribution of Podolsky and Pauling. To investigate the applicability of our results in an interpretation of electron-scattering experiments would be of considerable interest.

Further theoretical work has been undertaken using the momentum functions of Podolsky and Pauling to examine the momentum analogues of Hartree-Fock position space functions [19], as well as extension to molecular systems [20]. To our knowledge, no attempt has been made to explore the applicability of the momentum functions delineated here (see Eq. (33) and Appendix B) or previously [11]. Once again comparison of the two interpretations of momentum space would be definitely of interest.

In a comprehensive review, Thakkar [21] discussed much experimental and theoretical work in this field. Most pertinent to the discussion presented here, Thakkar obtained the radial momentum functions of Podolsky and Pauling as a Hankel transformation [22] over Bessel functions of half-integer order. Although this procedure produced a radial momentum distribution that seemed to fit the experimental data satisfactorily, it relies on angular functions that, although enabling those experimental fits, do not represent the properly chosen momentum variables. To test the observations presented here, it will be of considerable interest to develop experimental techniques to measure and to test the wave functions resulting from the viewpoint of momentum variables introduced here.

It is safe to say that, of the wave functions of atoms and molecules that have been obtained, the vast majority have been derived in position space. The explosion of interest in harnessing modern computers, coupled with advances in density-functional theory, have vastly increased the wealth of data that we have available on atoms and molecules through quantum calculations. These powerful techniques have, however, yet to be applied to momentum space as defined here. Even for the hydrogen atom, discussed here, considerable simplification of the expression and calculations of expectation values can be obtained. For example, in position space, the radial functions are expressed in

terms of Laguerre polynomials, whereas the corresponding functions in momentum space are simple sums over poles to varying orders. The latter have the advantage that integrals over these functions can be vastly simplified through the use of Cauchy's theorem [23]. Another simplification can occur on observing that the term for electron–electron repulsion, encountered in all multi-electron problems, becomes a momentum exchange operator in momentum space. The implications of this correspondence have yet to be explored. Furthermore, when effective functions in momentum space are obtained with modern techniques available through intensive computations, it is entirely

possible that a vast simplification of the functions might also be achievable. It might also be considered of some value to understand the other half of wave mechanics.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A

The harmonic oscillator in momentum space

We introduce the concepts with a simple and prototypical system, a canonical linear harmonic oscillator of mass μ and force coefficient k ; the amplitude function from a direct solution of the time-independent Schroedinger equation in terms of displacement coordinate q is expressed explicitly in this form containing Hermite polynomials H , with Planck constant h ,

$$\Psi_n(q) = \frac{2^{\frac{-2n+1}{4}}(k\mu)^{1/8}H\left(n, \sqrt{\frac{2\pi}{h}}(k\mu)^{1/2}q\right)e^{-\frac{\pi q^2\sqrt{k\mu}}{h}}}{\sqrt{n!}h^{1/4}} \tag{A1}$$

whereas the amplitude function from a direct solution of the time-independent Schroedinger equation in terms of momentum p has this explicit form of amplitude function, likewise containing Hermite polynomials,

$$\chi_n(p) = \frac{2^{\frac{-2n+1}{4}}H\left(n, \sqrt{\frac{2\pi}{h}}(k\mu)^{-1/2}p\right)e^{-\pi p^2/h\sqrt{k\mu}}}{\sqrt{n!}h^{1/4}(k\mu)^{1/8}} \tag{A2}$$

To convert amplitude functions $\Psi_n(q)$ in coordinate space into amplitude functions $\chi_n(p)$ in momentum space, one applies a Fourier transformation according to this relation,

$$\chi_n(p) = \int_{-\infty}^{\infty} \frac{\Psi_n(q)e^{-\frac{2\pi iqp}{h}}}{\sqrt{h}}dq \tag{A3}$$

which takes into account that the variable conjugate to q is not p but p/h ; the inverse Fourier transform, again with integration over all space of the system, is expressed as

$$\Psi_n(q) = \int_{-\infty}^{\infty} \frac{\chi_n(p)e^{\frac{2\pi iqp}{h}}}{\sqrt{h}}dp \tag{A4}$$

An extra factor i^n appears in amplitude functions transformed from relative to solved directly from Schroedinger's equation above; for applications this phase factor is inconsequential. These results constitute proof that a Fourier transform of an amplitude function in position space generates an amplitude function in momentum space, and vice versa. This symmetry between the solutions in position space and the solutions in momentum space arises from the nature of the Hamiltonian function in which terms in both momentum and position contribute quadratically to the energy. An observable property of a quantum–mechanical system is generated from an expectation value of the appropriate operator, such as o , calculated as an integral over the domain of the applicable variable, such as q or p , as

$$\langle o \rangle = \int_{-\infty}^{\infty} \Psi_n^*(q)o\Psi_n(q)dq \text{ or } \langle o \rangle = \int_{-\infty}^{\infty} \chi_n^*(p)o\chi(p)dp \tag{A5}$$

Appendix B

The angular part of the hydrogen atom in momentum space

We direct attention to the momentum analogues of the angular functions in position space. To maintain the correct uncertainty relations, we refine our selections of the conjugate variables, because the momentum variables corresponding to the angular variables (θ_p, ϕ_p) are Hermitian only in a space of functions with periods $\pi, 2\pi$, respectively. (θ_p, ϕ_p) are not, however, periodic; their domains are between 0 or $-\infty$ and ∞ . If we restrict θ and φ to run over $(0, \pi)$ and $(0, 2\pi)$, it is difficult to obtain physically meaningful uncertainty relations. This difficulty has been treated by several authors. [24–28] The problem becomes solvable on regarding variable θ_p to be conjugate to $u (= \cos(\theta))$ and ϕ_p conjugate to $v (= e^{i\varphi})$ instead of (θ, φ) . We thus consider variables (p, θ_p, ϕ_p) to be chosen conjugate to variables in the set (r, u, v) [11]. The square of the angular-momentum operator in position space is rewritten as

$$L^2 = (1 - u^2)\frac{\partial^2}{\partial u^2} - 2u\frac{\partial}{\partial u} + \frac{1}{1 - u^2}\left(v^2\frac{\partial^2}{\partial v^2} + v\frac{\partial}{\partial v}\right) \tag{B1}$$

We proceed with

$$\theta_p = -i\hbar\left(\frac{\partial}{\partial u}\right) \text{ and } \phi_p = -i\hbar\left(\frac{\partial}{\partial v}\right) \tag{B2}$$

$$u = i\hbar\left(\frac{\partial}{\partial \theta_p}\right) \text{ and } v = i\hbar\left(\frac{\partial}{\partial \phi_p}\right) \tag{B3}$$

Recalling that the angular eigenfunctions in the momentum representation are $\beta(\theta_p)\rho(\phi_p)$,

$$L^2\beta(\theta_p)\rho(\phi_p) = l(l+1)\hbar^2\beta(\theta_p)\rho(\phi_p) \tag{B4}$$

Separating variables, we obtain an equation for ρ as a quasi-Fourier transform,

$$\rho_m(\varphi_p) = \int_0^{2\pi} \Phi_m(\varphi)e^{i\varphi\varphi_p}d\varphi \tag{B5}$$

This equation has a complex solution,

$$\rho_m(\varphi_p) = \frac{-i(e^{2\pi i(\varphi_p+m)} - 1)}{2\pi(\varphi_p + m)} \tag{B6}$$

of which the real part is simply a sinc function, and is normalised such that

$$\int_{-\infty}^{\infty} \rho_m^*(\varphi_p)\rho_m(\varphi_p)d\varphi_p = 1 \tag{B7}$$

m must be an integer (positive, negative or zero).

With $g = \theta_p$ for the transformation from $\Theta(\theta)$, we solve the equation for β on defining function ω such that

$$\omega(\theta_p) = (1 - u^2)^{\frac{m}{2}}\beta_{l,m}(\theta_p) = \left(1 + \left(\frac{\partial^2}{\partial \theta_p^2}\right)\right)^{\frac{m}{2}}\beta_{l,m}(\theta_p) \tag{B8}$$

Using the transformation of Eqs. (26) and (27) we find

$$\left(\theta_p^2\left(\frac{\partial^2}{\partial \theta_p^2}\right) + 2(m+1)\theta_p\left(\frac{\partial}{\partial \theta_p}\right) + \theta_p^2 + m(m+1)\omega_{l,m}(\theta_p)\right) = l(l+1)\omega_{l,m}(\theta_p) \tag{B9}$$

The solution to this equation is expressed separately for $l - |m| = 2k$, with k integer, so even,

$$\begin{aligned} \beta_{l,m}(\theta_p) = & -\sqrt{\frac{i(2l+1)(l-|m|)!}{2(l+|m|)!}}2^{m|}\Gamma\left(\frac{1}{2}\right)\Gamma\left(\frac{|m|}{2}+1\right)\Gamma\left(\frac{|m|}{2}+\frac{1}{2}\right)\left(\frac{2}{\theta_p}\right)^{\left(\frac{|m|}{2}+\frac{1}{2}\right)}\sum_{k=0}^{(l-|m|)/2}\binom{4k+|m|+1}{2}(-i)^{2k}J\left(\frac{4k+|m|+1}{2},\theta_p\right) \\ & ph\left(\frac{-l+|m|}{2},k\right)ph\left(\frac{l+|m|+1}{2},k\right)ph\left(\frac{|m|}{2},\frac{l-|m|}{2}-k\right)ph\left(\frac{|m|+1}{2},k\right)ph\left(\frac{|m|+2}{2},k\right)(-1)^{(l-|m|-2k)/2}/\left(k!ph\left(\frac{1}{2},k\right)\right) \\ & ph\left(\frac{-l+|m|}{2},k\right)ph\left(\frac{l+|m|+2}{2},k\right)ph\left(\frac{|m|}{2},\frac{l-|m|-1}{2}-k\right)ph\left(\frac{|m|+3}{2},k\right)ph\left(\frac{|m|+2}{2},k\right)(-1)^{(l-|m|-1-2k)/2}/\left(k!ph\left(\frac{3}{2},k\right)\right) \end{aligned} \tag{B10}$$

whereas for $l - |m| = 2k + 1$, so an odd integer;

$$\begin{aligned} \beta_{l,m}(\theta_p) = & -\sqrt{\frac{i(2l+1)(l-|m|)!}{2(l+|m|)!}}2^{m|+1}\Gamma\left(\frac{1}{2}\right)\Gamma\left(\frac{|m|}{2}+1\right)\Gamma\left(\frac{|m|}{2}+\frac{3}{2}\right)\left(\frac{2}{\theta_p}\right)^{\left(\frac{|m|}{2}+\frac{1}{2}\right)}\sum_{k=0}^{(l-|m|-1)/2}\binom{4k+|m|+3}{2}(-i)^{2k+1}J\left(\frac{4k+|m|+3}{2},\theta_p\right) \\ & ph\left(\frac{-l+|m|+1}{2},k\right)ph\left(\frac{l+|m|+2}{2},k\right)ph\left(\frac{|m|}{2},\frac{l-|m|-1}{2}-k\right)ph\left(\frac{|m|+3}{2},k\right)ph\left(\frac{|m|+2}{2},k\right)(-1)^{(l-|m|-1-2k)/2}/\left(k!ph\left(\frac{3}{2},k\right)\right) \\ & ph\left(\frac{l+4}{2},k\right)/\left(\Gamma\left(\frac{l-|m|+1}{2}\right)\right)\Gamma\left(-\frac{l+|m|}{2}\right)\Gamma\left(\frac{l}{2}+2\right) \end{aligned} \tag{B11}$$

These formulae that contain Bessel function J and Pochhammer function ph (expressed here as $ph(x,y)$ but commonly written $(x)_y$, equal to $\Gamma(x+y)/\Gamma(y)$ in either case) are fully normalised according to

$$\int_0^{\infty} \beta_{l,m}(\theta_p)^*\beta_{l,m}(\theta_p)d\theta_p = 1 \tag{B12}$$

These solutions are also obtainable directly from this quasi-Fourier transform,

$$\beta_{l,m}(\theta_p) = \frac{i+1}{\sqrt{2\pi}}\int_{-1}^1 \theta(x)e^{ix\theta_p}dx \tag{B13}$$

in which $x = \cos(\theta)$; the quantity $\frac{i+1}{\sqrt{2\pi}}$ is a normalising factor.

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