

Fock transforms in reciprocal-space quantum theory

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Received 24 June 1993

In Fock's reciprocal-space treatment of the hydrogen atom, k -space is mapped onto the surface of a 4-dimensional hypersphere, and the solutions (apart from an invariant factor) are 4-dimensional hyperspherical harmonics. Fock's method can be generalized to provide solutions for the Schrödinger equation of a charged particle moving in a many-center Coulomb potential, and in this case the solutions are found by diagonalizing an overlap matrix involving products of hyperspherical harmonics. The present paper discusses a transform which can conveniently be used to evaluate the elements of the overlap matrix.

1. Introduction

Hyperspherical harmonics are eigenfunctions of the generalized angular momentum operator

$$\Lambda^2 Y_{\lambda\mu} = \lambda(\lambda + d - 2) Y_{\lambda\mu}, \quad \lambda = 0, 1, 2, \dots,$$

$$\Lambda^2 \equiv - \sum_{i>j}^d \left(x_i \frac{\partial}{\partial x_j} - x_j \frac{\partial}{\partial x_i} \right)^2. \quad (1)$$

In eq. (1) we have used a notation which emphasizes the similarity between the hyperspherical harmonics $Y_{\lambda\mu}$ and the spherical harmonics Y_{lm} . However, in the d -dimensional case, μ is not a single index but stands for a set of indices representing eigenvalues of a complete set of operators which commute with Λ^2 and with each other. The choice of these operators is not unique, but in physical applications it is convenient to choose the set which commutes with the Hamiltonian of the system. Table 1 shows the first few hyperspherical harmonics for $d = 4$. (As we shall see below, the 4-dimensional hyperspherical harmonics play an important role in reciprocal-space quantum theory.) The index μ of eq. (1) stands for the two indices l and m in table 1. If the angles χ , θ and ϕ are related to the unit vectors in a 4-dimensional space by

$$u_1 = \sin \chi \sin \theta \cos \phi,$$

Table 1
4-dimensional hyperspherical harmonics and their associated hydrogenlike orbitals.

λ	l	m	$Y_{\lambda lm}$	$\psi_{\lambda lm}(\mathbf{r})$
0	0	0	$\frac{1}{\pi\sqrt{2}}$	$\sqrt{\frac{k_0^3}{\pi}}e^{-t}$
1	0	0	$\frac{\sqrt{2}}{\pi}u_4$	$\sqrt{\frac{k_0^3}{\pi}}e^{-t}(1-t)$
1	1	1	$-\frac{i}{\pi}(u_1 + iu_2)$	$-\sqrt{\frac{k_0^3}{2\pi}}e^{-t}(t_1 + it_2)$
1	1	0	$\frac{i\sqrt{2}}{\pi}u_3$	$\sqrt{\frac{k_0^3}{\pi}}e^{-t}t_3$
1	1	-1	$\frac{i}{\pi}(u_1 - iu_2)$	$\sqrt{\frac{k_0^3}{2\pi}}e^{-t}(t_1 - it_2)$

$$u_2 = \sin \chi \sin \theta \sin \phi,$$

$$u_3 = \sin \chi \cos \theta,$$

$$u_4 = \cos \chi, \quad (2)$$

then the 4-dimensional hyperspherical harmonics can be written explicitly in the form

$$\phi_{\lambda}(\mathbf{u}) = Y_{\lambda lm}(\mathbf{u}) = i^l N \sin^l \chi C_{\lambda-l}^{1+l}(\cos \chi) Y_{lm}(\theta_k, \phi_k), \quad (3)$$

where

$$N = \sqrt{\frac{2(2l)!!(\lambda+1)(\lambda-l)!(2l+1)!}{\pi(2l+1)!!(\lambda+l+1)!}}, \quad (4)$$

and where C_{λ}^{α} is a Gegenbauer polynomial defined by

$$C_{\lambda}^{\alpha}(\mathbf{u} \cdot \mathbf{u}') = \frac{1}{\Gamma(\alpha)} \sum_{t=0}^{[\lambda/2]} \frac{(-1)^t \Gamma(\alpha + \lambda - t) (2\mathbf{u} \cdot \mathbf{u}')^{\lambda-2t}}{t!(\lambda-2t)!}. \quad (5)$$

(In the theory of hyperspherical harmonics, Gegenbauer polynomials play a role analogous to that played by Legendre polynomials in the familiar theory of spherical harmonics; and when $\alpha = 1/2$, the Gegenbauer polynomials reduce to Legendre polynomials.)

Each of the familiar properties of spherical harmonics has a d -dimensional generalization; and it may be useful here to mention briefly a few of these properties. The interested reader can find the theory of hyperspherical harmonics developed in more detail in refs. [1] and [2].

The familiar expansion of the Green's function of the Laplacian operator in terms of Legendre polynomials:

$$\frac{1}{|\mathbf{x} - \mathbf{x}'|} = \frac{1}{r_{>}} \sum_{l=0}^{\infty} \left(\frac{r_{<}}{r_{>}}\right)^l P_l(\mathbf{u} \cdot \mathbf{u}') \tag{6}$$

has a d -dimensional generalization:

$$\frac{1}{|\mathbf{x} - \mathbf{x}'|^{d-2}} = \frac{1}{r_{>}^{d-2}} \sum_{\lambda=0}^{\infty} \left(\frac{r_{<}}{r_{>}}\right)^{\lambda} C_{\lambda}^{\alpha}(\mathbf{u} \cdot \mathbf{u}'), \tag{7}$$

where C_{λ}^{α} is a Gegenbauer polynomial, $\alpha = d/2 - 1$ and where \mathbf{u} and \mathbf{u}' are unit vectors in the directions of the d -dimensional vectors \mathbf{x} and \mathbf{x}' .

The hyperspherical harmonics obey a sum rule involving Gegenbauer polynomials:

$$\sum_{\mu} Y_{\lambda\mu}^*(\mathbf{u}') Y_{\lambda\mu}(\mathbf{u}) = \frac{(2\lambda + d - 2)}{(d - 2)I(0)} C_{\lambda}^{\alpha}(\mathbf{u} \cdot \mathbf{u}'), \tag{8}$$

where

$$\int d\Omega = \frac{2\pi d/2}{\Gamma(\frac{d}{2})} \equiv I(0) \tag{9}$$

is the total solid angle, and where the sum \sum_{μ} is taken over all the eigenfunctions of Λ^2 corresponding to the eigenvalue $\lambda(\lambda + d - 2)$. This sum rule is the generalization of the familiar sum rule for spherical harmonics:

$$\sum_m Y_{lm}^*(\mathbf{u}') Y_{lm}(\mathbf{u}) = \frac{2l + 1}{4\pi} P_l(\mathbf{u} \cdot \mathbf{u}'). \tag{10}$$

From eq. (8) it follows that

$$\begin{aligned} O_{\lambda}[F(\mathbf{u})] &\equiv \sum_{\mu} Y_{\lambda\mu}(\mathbf{u}) \int d\Omega' Y_{\lambda\mu}^*(\mathbf{u}') F(\mathbf{u}') \\ &= \frac{2\lambda + d - 2}{(d - 2)I(0)} \int d\Omega' C_{\lambda}^{\alpha}(\mathbf{u} \cdot \mathbf{u}') F(\mathbf{u}') \end{aligned} \tag{11}$$

is the component of $F(\mathbf{u}')$ which is an eigenfunction of Λ^2 with the eigenvalue $\lambda(\lambda + d - 2)$.

The degeneracy of the hyperspherical harmonics (i.e. the number of linearly independent eigenfunctions of Λ^2 corresponding to a particular value of λ) can be shown to be

$$\omega = \frac{(d + 2\lambda - 2)(\lambda + d - 3)!}{\lambda!(d - 2)!}. \quad (12)$$

When $d = 3$ and $\lambda = l$, this becomes

$$\omega = 2l + 1, \quad (13)$$

while when $d = 4$, we have

$$\omega = (\lambda + 1)^2. \quad (14)$$

2. The hydrogen atom in reciprocal space

When $d = 4$, the number of linearly independent hyperspherical harmonics belonging to a given value of λ is $(\lambda + 1)^2$, i.e., 1, 4, 9, 16, ..., and so on – exactly the same as the degeneracy of the solutions to the Schrödinger equation for a hydrogen atom. V. Fock was, in fact, able to show that the Fourier transforms of the hydrogen atom wave functions can be written in the form [3]

$$\psi_{n,l,m}^l(\mathbf{k}) = M(k) Y_{n-1,l,m}(\mathbf{u}), \quad (15)$$

where Ω is the solid angle in a 4-dimensional space defined by the unit vectors

$$\begin{aligned} u_1 &= \frac{2k_0k_1}{k_0^2 + k^2} = \sin \chi \sin \theta \cos \phi, \\ u_2 &= \frac{2k_0k_2}{k_0^2 + k^2} = \sin \chi \sin \theta \sin \phi, \\ u_3 &= \frac{2k_0k_3}{k_0^2 + k^2} = \sin \chi \cos \theta, \\ u_4 &= \frac{k^2 - k_0^2}{k_0^2 + k^2} = \cos \chi, \end{aligned} \quad (16)$$

and where $k_0^2 = -2E$. The function $M(k)$ is independent of the quantum numbers and is given by

$$M(k) = \frac{4k_0^{5/2}}{(k_0^2 + k^2)^2}. \quad (17)$$

Fock's derivation of this result, expressed briefly, is as follows: The Fourier transformed Schrödinger equation for a hydrogen atom is an integral equation which can be written in the form

$$(k_0^2 + k'^2)^2 \psi'(\mathbf{k}') = \frac{Z}{2k_0\pi^2} \int d\Omega \frac{(k_0^2 + k^2)2\psi'(\mathbf{k})}{|\mathbf{u} - \mathbf{u}'|^2}, \tag{18}$$

where \mathbf{u} and \mathbf{u}' are unit vectors of the form shown in eq. (16). The integral over $d\Omega$ is an integral over solid angle in a 4-dimensional space defined by these vectors. In other words, Fock's transformation, eq. (16), maps the 3-dimensional \mathbf{k} -space onto the surface of a hypersphere in a 4-dimensional space. If we let

$$\psi'(\mathbf{k}) = \frac{4k_0^{5/2}}{(k_0^2 + k^2)^2} \phi(\mathbf{u}), \tag{19}$$

then (18) takes on the simple form

$$\phi(\mathbf{u}') = \frac{Z}{2\pi^2 k_0} \int d\Omega \frac{1}{|\mathbf{u} - \mathbf{u}'|^2} \phi(\mathbf{u}). \tag{20}$$

From eq. (7) with $d = 4$ and $\alpha = 1$, we have

$$\frac{1}{|\mathbf{u} - \mathbf{u}'|^2} = \sum_{\lambda=0}^{\infty} C_{\lambda}^1(\mathbf{u} \cdot \mathbf{u}') \tag{21}$$

so that (20) becomes

$$\phi(\mathbf{u}') = \frac{Z}{2\pi^2 k_0} \sum_{\lambda=0}^{\infty} \int d\Omega C_{\lambda}^1(\mathbf{u} \cdot \mathbf{u}') \phi(\mathbf{u}). \tag{22}$$

But from (11) we have

$$\int d\Omega C_{\lambda}^1(\mathbf{u} \cdot \mathbf{u}') \phi(\mathbf{u}) = \frac{(d-2)I(0)}{\lambda + d - 2} O_{\lambda}[\phi(\mathbf{u}')], \tag{23}$$

where O_{λ} is a projection operator corresponding to the λ th eigenvalue of Λ^2 . When $d = 4$,

$$\frac{(d-2)I(0)}{\lambda + d - 2} = \frac{2\pi^2}{\lambda + 1}. \tag{24}$$

Thus we can rewrite (22) in the form

$$\phi(\mathbf{u}) = \sum_{\lambda'=1}^{\infty} \frac{Z}{k_0(\lambda' + 1)} O_{\lambda'}[\phi(\mathbf{u})]. \tag{25}$$

If we let

$$\phi(\mathbf{u}) = Y_{\lambda\mu}(\mathbf{u}), \tag{26}$$

then (25) becomes

$$Y_{\lambda\mu}(\mathbf{u}) = \frac{Z}{k_0(\lambda + 1)} Y_{\lambda\mu}(\mathbf{u}), \tag{27}$$

which will be satisfied if

$$\frac{Z}{k_0(\lambda + 1)} = 1. \quad (28)$$

Remembering that $k_0^2 = -2E$, and identifying $\lambda + 1$ with n , we have

$$E = -\frac{Z^2}{2n^2} \quad (29)$$

in agreement with the usual direct-space solution of the hydrogen atom problem. With the choice of phases shown in eq. (3) and (16), Fock's reciprocal-space solutions are related to the direct-space solutions through a Fourier transform

$$\frac{1}{(2\pi)^{3/2}} \int d^3k e^{ik \cdot x} \frac{4k_0^{5/2}}{(k_0^2 + k^2)^2} Y_{n-1,l,m}(\mathbf{u}) = R_{nl}(r) Y_{lm}(\theta, \phi), \quad (30)$$

where

$$R_{nl} = (2k_0)^{3/2} \mathcal{N} t^l e^{-t} F(l+1-n|2l+2|2t), \quad (31)$$

$$t \equiv k_0 r \quad (32)$$

and

$$\mathcal{N} \equiv \frac{2^l}{(2l+1)!} \sqrt{\frac{(l+n)!}{2n(n-l-1)!}}. \quad (33)$$

3. Many-center Coulomb potentials

It has been shown by a number of authors [4–6] that Fock's approach can be generalized in such a way as to yield solutions to the reciprocal-space Schrödinger equation for a charged particle moving in the many-center potential:

$$V(\mathbf{x}) = -\sum_j Z_j \frac{1}{|\mathbf{x} - \mathbf{R}_j|}. \quad (34)$$

If we again let the Fourier-transformed wave function, $\psi^l(\mathbf{k})$ be represented by eq. (19), then the equation analogous to (28) becomes

$$\phi(\mathbf{u}') = \frac{1}{2\pi^2 k_0} \sum_j Z_j \int d\Omega \frac{e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{R}_j}}{|\mathbf{u} - \mathbf{u}'|^2} \phi(\mathbf{u}). \quad (35)$$

If we let

$$\eta_r(\mathbf{u}) \equiv \eta_{j\lambda lm}(\mathbf{u}) \equiv \left(\frac{Z_j}{\lambda+1}\right)^{1/2} e^{i\mathbf{k} \cdot \mathbf{R}_j} Y_{\lambda lm}(\mathbf{u}) \quad (36)$$

and make use of eqs. (21) and (8), we can rewrite (35) in the form

$$k_0\phi(\mathbf{u}') = \sum_{\tau} \eta_{\tau}(\mathbf{u}') \int d\Omega \eta_{\tau}^*(\mathbf{u})\phi(\mathbf{u}). \tag{37}$$

The functions $\eta_{\tau}(\mathbf{u})$ are not orthonormal, and we can let the matrix

$$K_{\tau,\tau'} \equiv \left(\frac{Z_j Z_{j'}}{(\lambda + 1)(\lambda' + 1)} \right)^{1/2} \int d\Omega e^{i\mathbf{k}\cdot(\mathbf{R}_{j'} - \mathbf{R}_j)} Y_{\lambda lm}^*(\mathbf{u}) Y_{\lambda' l' m'}(\mathbf{u}) \tag{38}$$

represent the overlap matrix between them. If we represent the solutions to (35) by a linear combination of the basis functions, so that

$$\phi(\mathbf{u}) = \sum_{\tau} \eta_{\tau}(\mathbf{u})B_{\tau}, \tag{39}$$

then (37) becomes

$$k_0 \sum_{\tau} \eta_{\tau}(\mathbf{u}')B_{\tau} = \sum_{\tau,\tau'} \eta_{\tau}(\mathbf{u}')K_{\tau,\tau'}B_{\tau'}. \tag{40}$$

From the fact that the basis functions are linearly independent, it follows that the expansion coefficients must be solutions to the secular equations

$$\sum_{\tau'} [K_{\tau,\tau'} - \delta_{\tau,\tau'}k_0]B_{\tau'} = 0. \tag{41}$$

As a simple example to illustrate this method, we can consider an electron in the field of two nuclei with charges Z_1 and Z_2 . In the lowest approximation, we can represent $\phi(\mathbf{u})$ by a linear combination of two basis functions, both with $\lambda = 0$:

$$\phi(\mathbf{u}) \approx \eta_1(\mathbf{u})B_1 + \eta_2(\mathbf{u})B_2, \tag{42}$$

where

$$\begin{aligned} \eta_1(\mathbf{u}) &= \sqrt{Z_1} e^{i\mathbf{k}\cdot\mathbf{R}_1} Y_{000} = \frac{1}{\pi} \sqrt{\frac{Z_1}{2}} e^{i\mathbf{k}\cdot\mathbf{R}_1}, \\ \eta_2(\mathbf{u}) &= \sqrt{Z_2} e^{i\mathbf{k}\cdot\mathbf{R}_2} Y_{000} = \frac{1}{\pi} \sqrt{\frac{Z_2}{2}} e^{i\mathbf{k}\cdot\mathbf{R}_2}. \end{aligned} \tag{43}$$

Using methods which will be discussed in the next section, we find that

$$\frac{1}{2\pi^2} \int d\Omega e^{i\mathbf{k}\cdot(\mathbf{R}_1 - \mathbf{R}_2)} = (1 + t)e^{-t}, \tag{44}$$

where

$$t \equiv k_0|\mathbf{R}_1 - \mathbf{R}_2| \equiv k_0R_{12}. \tag{45}$$

Thus

$$K_{\tau,\tau'} = \begin{pmatrix} Z_1 & \sqrt{Z_1 Z_2}(1 + t)e^{-t} \\ \sqrt{Z_1 Z_2}(1 + t)e^{-t} & Z_2 \end{pmatrix}, \tag{46}$$

so that the secular equations, (41), require that k_0 and R_{12} satisfy

$$2k_0 = Z_1 + Z_2 \pm \sqrt{(Z_1 + Z_2)^2 + 4Z_1Z_2[(1+t)^2e^{-2t} - 1]},$$

$$R_{12} = \frac{t}{k_0}. \quad (47)$$

Letting the parameter t run from 0 to ∞ , we can generate values of k_0 and $E = -k_0^2/2$ and the values of R_{12} to which they correspond. In the limit $t = 0$ (and $R_{12} = 0$), we obtain the exact ground-state united-atom energy:

$$k_{0+} = Z_1 + Z_2, \quad E_+ = -\frac{(Z_1 + Z_2)^2}{2}, \quad (48)$$

while for $t = \infty$, we obtain the exact separated-atom energies:

$$k_{0+} = Z_1, \quad E_+ = -\frac{Z_1^2}{2},$$

$$k_{0-} = Z_2, \quad E_- = -\frac{Z_2^2}{2}. \quad (49)$$

For intermediate values of t , the energies found from the approximate wave function (42) differ appreciably from the exact energies. However, when a larger number of basis functions are used, the method outlined above is capable of great accuracy. Koga and Matsushashi, for example, were able to obtain 10-figure accuracy by this method in calculations on the H_2^+ ion [7].

As a second simple example, we can consider the orbital of an electron in the field of three nuclei. If we again use only basis functions with $\lambda = 0$, the overlap matrix becomes

$$K_{\tau,\tau'} = \begin{pmatrix} Z_1 & \sqrt{Z_1Z_2}(1+t)e^{-t} & \sqrt{Z_1Z_3}(1+t')e^{-t'} \\ \sqrt{Z_1Z_2}(1+t)e^{-t} & Z_3 & \sqrt{Z_2Z_3}(1+t'')e^{-t''} \\ \sqrt{Z_1Z_3}(1+t')e^{-t'} & \sqrt{Z_2Z_3}(1+t'')e^{-t''} & Z_3 \end{pmatrix}, \quad (50)$$

where $t \equiv k_0R_{12}$, $t' \equiv k_0R_{13}$, and $t'' \equiv k_0R_{23}$. By diagonalizing this matrix for values of the parameters t , t' and t'' running from 0 to ∞ , we obtain the orbitals and energies as functions of the internuclear distances.

4. Fock transforms

From the discussion given above, we can see that integrals of the form

$$S_{n'l'm'}^{nlm}(\mathbf{R}) \equiv \int d\Omega e^{i\mathbf{k}\cdot\mathbf{R}} Y_{n'-1,l',m'}^*(\mathbf{u}) Y_{n-1,l,m}(\mathbf{u}) \quad (51)$$

are of great importance in reciprocal-space quantum theory. In fact, as Monkhorst and Jeriorski have pointed out [4], the many-center one-particle Coulomb problem in reciprocal space reduces essentially to the problem of evaluating these integrals. In an early paper [4], Shibuya and Wulfman developed a method for their evaluation based on the R_4 Wigner coefficients. In this paper we shall discuss an alternative method based on a transform defined by the relationship

$$\frac{1}{2\pi^2} \int d\Omega e^{ik \cdot R} f(\mathbf{u}) = \tilde{f}(\mathbf{t}) \tag{52}$$

with $\mathbf{t} \equiv k_0 \mathbf{R}$. To honour the pioneering work of Fock, we might call this a *Fock transform*.

The solid-angle element in 4-dimensional space is given by

$$d\Omega = \sin^2 \chi \sin \theta \, d\chi \, d\theta \, d\phi, \tag{53}$$

where χ, θ and ϕ are defined by eq. (16). Since (from eq. (16))

$$\sin \chi = \frac{2k_0 k}{k_0^2 + k^2}, \tag{54}$$

the solid-angle element can be written in the form

$$d\Omega = \left(\frac{2k_0}{k_0^2 + k^2} \right)^3 k^2 \sin \theta \, dk \, d\theta \, d\phi = \left(\frac{2k_0}{k_0^2 + k^2} \right)^3 d^3 k. \tag{55}$$

From (16) it also follows that

$$1 - u_4 = \frac{2k_0^2}{k_0^2 + k^2}. \tag{56}$$

Using eqs. (3), (55) and (56), together with the ratio

$$\frac{\mathcal{N}}{\mathcal{N}'} = \frac{2^l (n+l)! \sqrt{\pi}}{(n-l-1)! (2l+1)! 2n(2l)!!} \tag{57}$$

of the normalization constants defined in eqs. (4) and (33), we can rewrite (30) in the form:

$$\begin{aligned} & \frac{1}{2\pi^2} \int d\Omega e^{ik \cdot R} \frac{1}{1-u_4} C_{n-l-1}^{l+1}(u_4) h_l(u_j) \\ &= \frac{2(n+l)! e^{-t} F(l+1-n|2l+2|2t) h_l(t_j)}{i^l (2l+1)! l! n(n-l-1)!}. \end{aligned} \tag{58}$$

In (58),

$$h_l(t_j) \equiv t^l Y_{lm}(\theta_t, \phi_t) \tag{59}$$

is an harmonic polynomial in t_1, t_2 , and t_3 , where $\mathbf{t} \equiv k_0 \mathbf{R}$, while $h_l(u_j)$ is the same harmonic polynomial as a function of u_1, u_2 , and u_3 . The information contained in eq. (58) can be expressed in a more convenient form by using the relationship [8]

$$u_4^p = \frac{l!p!}{2^p} \sum_{s=0}^{\lfloor p/2 \rfloor} \frac{(p+l+1-2s)}{s!(p+l+1-s)!} C_{p-2s}^{l+1}(u_4). \tag{60}$$

Combining (58) and (59) we obtain the Fock transform of $u_4^p h_l(u_j)$:

$$\begin{aligned} & \frac{1}{2\pi^2} \int d\Omega e^{ik \cdot R} u_4^p h_l(u_j) \\ &= \frac{p!e^{-t}h_l(t_j)}{2^p i^l (2l+1)!} \left[\sum_{s=0}^{\lfloor p/2 \rfloor} \frac{2(p+2l+1-2s)!F(2s-p|2l+2|2t)}{s!(p+l+1-s)!(p-2s)!} \right. \\ & \quad \left. - (p+1) \sum_{s=0}^{\lfloor (p+1)/2 \rfloor} \frac{(p+2+2l-2s)!F(2s-p-1|2l+2|2t)}{s!(p+2+l-s)!(p+1-2s)!} \right], \end{aligned} \tag{61}$$

where p is an integer and where h_l is an arbitrary harmonic polynomial of order l . Particular examples of the transforms of eq. (61) are shown in tables 2 and 3.

5. Discussion

Equation (61) allows us to evaluate Fock transforms of functions of the form $u_4^p h_l(u_j)$, where p is an integer and $h_l(u_j)$ is an harmonic polynomial of order l in u_1, u_2 , and u_3 , i.e., where h_l is a homogeneous polynomial of order l satisfying

$$\sum_{j=1}^3 \frac{\partial^2}{\partial u_j^2} h_l = 0. \tag{62}$$

However, in order to evaluate the overlap integrals needed in reciprocal-space quantum theory, we still need to relate these transforms to integrals of the form shown in eq. (51). In simple cases, we can do this by hand, but in more complicated cases, it is convenient to have a computer program to perform the necessary

Table 2
Fock transforms.

$f(u)$	$\frac{1}{2\pi^2} \int d\Omega e^{ik \cdot R} f(u)$
$h_l(u_j)$	$\frac{2e^{-t}(1+t)}{i^l(l+2)!} h_l(t_j)$
$u_4 h_l(u_j)$	$\frac{2e^{-t}(l+lt-t^2)}{i^l(l+3)!} h_l(t_j)$
$u_4^2 h_l(u_j)$	$\frac{2e^{-t}[(l^2+l+3)(1+t) - (2l+2)t^2 + t^3]}{i^l(l+4)!} h_l(t_j)$

Table 3
Fock transforms.

$f(\mathbf{u})$	$\frac{1}{2\pi^2} \int d\Omega e^{i\mathbf{k}\cdot\mathbf{R}} f(\mathbf{u})$
1	$e^{-t}(1+t)$
u_1	$\frac{2}{3!i} e^{-t}(1+t)t_1$
$u_1 u_2$	$\frac{2}{4!i^2} e^{-t}(1+t)t_1 t_2$
$u_1 u_2 u_3$	$\frac{2}{5!i^3} e^{-t}(1+t)t_1 t_2 t_3$
u_4	$-\frac{1}{3} e^{-t} t^2$
$u_4 u_1$	$\frac{1}{12i} e^{-t}(1+t-t^2)t_1$
u_4^2	$\frac{1}{6} e^{-t}(3+3t-2t^2+t^3)$

algebraic operations. My co-worker, Frank Antonsen, and I have developed a computer program for performing algebraic operations on polynomials in many-dimensional spaces. In this program, a polynomial of the form

$$f_a(\mathbf{x}) \equiv \sum_{j=1}^m a_j x_1^{n_1} x_2^{n_2} \dots x_d^{n_d} \tag{63}$$

is stored as an array of complex numbers, $a(j), j = 1, \dots, m$, and an array of integers, $n(k, j), k = 1, \dots, d, j = 1, \dots, m$. The program calculates products, sums, differentials and so on by carrying out the appropriate operations on these arrays. From these elementary operations, the program builds up more complicated ones, such as harmonic projection [2]. Our program is thus able to calculate integrals of the form shown in eq. (51) from the Fock transforms of eq. (61), thus avoiding the use of 4-dimensional Wigner coefficients. More generally, our program offers an alternative to the use of group-theoretical coupling coefficients in all problems involving angular or hyperangular functions.

The reciprocal-space form of the Schrödinger equation (with k -space projected onto the surface of a hypersphere) is less familiar than the usual direct-space form. However, in many applications, reciprocal-space quantum theory may offer advantages because of the simplicity of the wave functions. An interesting feature of the k -space secular equations (41) is that the roots are not energies but are instead Slater exponents of the optimal wave functions for representing particular states. The basis sets in this formulation are of the Sturmian type, i.e. they all

correspond to the same energy, $E = -k_0^2/2$, irrespective of the quantum numbers [9–12]. The constancy of the energy corresponds to constancy of the radius of the hypersphere onto which k -space is projected by the Fock transformation. In the present paper, we have discussed the one-particle many-center Coulomb problem, but analogous methods may be used to treat many-particle problems [12]. Because of the promising results already obtained using these methods, it seems likely that in the future they will prove to be very useful in quantum-chemistry.

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