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NON-INVARIANCE GROUPS IN PHYSICS AND CHEMISTRY: THE $O(f, 2)$ ALGEBRA AND THE SPHERICAL HARMONICS IN f DIMENSIONS*

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This article is dedicated to Mexican Science and to Professor Marcos Moshinsky and the late Elena Moshinsky, who did so much for it as a team.

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ABSTRACT: The concept of a non-invariance group is presented by constructing a Lie algebra representation of the non-compact group $O(f, 2)$ on the f-dimensional spherical harmonics. Applications of the analysis are made on the bound state Kepler problem in $f-1$ dimensions, and by constructing the angular portion of the dipole operator with the generators of the $O(f, 2)$ algebra. Uses of non-invariance groups in chemistry are discussed.

INTRODUCTION

The use of group theory in quantum chemistry has been limited for the most part to invariance groups, in which all of the group elements commute with the hamiltonian of the system of interest. Thus, most chemists are familiar with the uses of the three-dimensional rotation group for quantizing orbital angular momentum, $SU(2)$ for describing spin properties, and of course, the finite point groups which characterize most molecular systems. Perhaps less familiar is the concept of a *dynamical, non-invariance* group for a hamiltonian H. Such a group contains elements which do not commute with H, and thus necessarily connect states of different energies. Irreducible representations of a non-invariance group may contain all or part of the spectrum of H, and are useful for classification of the states. (For an early discussion of examples of dynamical groups that are applicable to molecular spectra see ref.(1)). In addition, quantities of physical interest such as the dipole operator may possibly be represented as a simple function of the group elements, or as a tensor operator, leading to a simplification in the evaluation of matrix elements and the appearance of selection rules. We have included several references[1-8] in which the uses of dynamical groups have been discussed with regard to problems of chemical interest, although this list is by no means complete. Reference (4) presents a very elegant and fundamental treatment of the higher groups in quantum as well as classical mechanics.

The concept of a non-invariance group in atomic physics is well understood for simple systems. For instance, it was shown by Fock[9] that the four-dimensional rotation group was the invariance group of the bound state hydrogen atom which explains the degeneracy of states having the same principal quantum number. Yet more recently it has been shown[10, 11] that a non-invariance group $O(4, 2)$ contains operators which can generate the entire bound state spectrum, and may be used to construct a group theoretical representation of the dipole operator as well.

In the present paper we shall use the spherical harmonics in f-dimensions to show that there is a representation of a group locally isomorphic to $O(f, 2)$ which is a non-invariance group for the usual $O(f)$ rotation group. We confine our analysis not to the full group representation, but rather to the more useful Lie algebra representation. It has been known for some time[12-17] that the representation of Lie algebras on spaces of orthogonal functions is related to the ladder operators in the factorization method of Infeld and Hull[18]. As such, the present analysis could be regarded as an application of this relationship. It is hoped that our simple application may serve as a useful introduction to non-invariance groups, and in the case of $O(f, 2)$ to the representation of non-compact groups of infinite dimensional vector spaces.

In section I we review briefly the properties of the spherical harmonics, which are bases for irreducible representations of the angular momentum group $O(f)$. In section II we use ladder operators, known from the factorization method, to show that the spherical harmonics in an f-dimensional space are a basis for a representation of a Lie algebra locally isomorphic to $O(f, 2)$, if $f \geqslant 3$. This algebra will be denoted as the "angular" $O(f, 2)$. The two dimensional space is considered separately in section III, and it is shown to be related to the $O(2,1)$ algebra. In section IV we review the relationship of the $(f + 1)$ dimensional spherical harmonics to the non-relativistic Kepler problem in f dimensions, and show that the bound state eigenfunctions are a basis for a representation of $O(f + 1, 2)$, a result which we have noted for $f = 3$. In section V the angular portion of the f-dimensional dipole operator is constructed with the generators of the "angular" $O(f, 2)$ generators.

Our interest in the angular $O(f, 2)$ stems from our investigation[5] of the bound state hydrogen atom radial functions, which were shown to be a basis for a Lie algebra representation isomorphic to $O(3, 2)$. The results of the present work indicate that the Lie algebra description of the full wave functions is contained in the product representation $O(3,2)_{\text{Radial}} \otimes O(3, 2)_{\text{Angular}}$ of radial and angular wavefunctions.

I. THE SPHERICAL HARMONICS IN f DIMENSIONS

The properties of angular momentum on f dimensions are too familiar to warrant a detailed discussion[19], but for notational convenience we shall review the more important aspects briefly. The Lie algebra of the f-dimensional rotation group is generated by the $f(f-1)/2$ operators

$$L_{jk} = x_j p_k - x_k p_j \quad (j, k = 1, 2, \ldots, f). \tag{1}$$

The f-dimensional spherical harmonics are the eigenfunctions of the f-1 operators

$$L_t^2 = \tfrac{1}{2} \sum_{j,k=1}^{t} L_{jk}^2 \quad (t = 2, 3, \ldots, f). \tag{2}$$

The corresponding integer eigenvalues are $l_t(l_t + t - 2)$, with $0 \leq |l_2| \leq l_3 \leq \ldots \leq l_f$. In hyperspherical coordinates the operator L_t^2 becomes

$$L_t^2 = -\frac{1}{\sin\theta_t}\frac{d}{d\theta_t}(\sin\theta_t \frac{d}{d\theta_t}) - (t-3)\cot\theta_t \frac{d}{d\theta_t} + \frac{L_{t-1}^2}{\sin^2\theta_t}. \tag{3}$$

If L_{t-1}^2 is replaced by its eigenvalue $l_{t-1}(l_{t-1} + t - 3)$ we can define the functions $A_{l_t l_{t-1}}^{(t)}$ to be the solutions of the equation

$$[L_t^2 - l_t(l_t + t - 2)]\, A_{l_t l_{t-1}}^{(t)} = 0 . \tag{4}$$

The f-dimensional spherical harmonics, denoted by $Y_{l_f, l_{f-1}, \ldots l_2}$, or simply $Y_{l_f}^{(f)}$, may then be defined in terms of the $(f-1)$-dimensional spherical harmonics by the formula

$$Y_{lf}^{(f)} = A_{l_f l_{f-1}}^{(f)} Y_{l_{f-1}}^{(f-1)} . \tag{5}$$

The solutions of (4) for $f > 2$ are

$$A_{kl}^{(f)} = N_{klf}(\sin\theta_f)^l F(l-k, l+k+f-2; l+\frac{f-1}{2}; \frac{1-\cos\theta_f}{2}), \tag{6}$$

with

$$N_{klf} = C_{kl}\left\{\frac{\Gamma(l+k+f-2)\,[k+\tfrac{1}{2}(f-2)]}{\Gamma(k-l+1)\,\Gamma\,[l+\tfrac{1}{2}(f-1)]^2\,2^{2l+f-3}}\right\}^{\frac{1}{2}} \tag{7}$$

The indices l_f and l_{f-1} in (4) have been replaced by k and l for convenience. C_{kl} is an arbitrary phase factor. In this paper we shall use $C_{kl} = (-)^{\frac{1}{2}(l+|l|)}$ so that for $f = 3$ our results are consistent with the usual Condon-Shortley phase convention[20]. The normalization constant N_{klf} is chosen so that

$$\int_0^{\pi} A_{kl}^{(f)*}\, A_{k'l}^{(f)}\,(\sin\theta_f)^{f-2}\, d\theta_f = \delta_{k,k'} \ . \tag{8}$$

The spherical harmonics in two dimensions will be discussed in section III.

For a fixed value of f the different $A_{kl}^{(f)}$ are related to each other by means of the following ladder operators:

$$G_{\pm} = \pm\,\frac{d}{d\theta_f} - \cot\theta_f\,(G \pm \frac{f-3}{2}) \ , \tag{9a}$$

$$N_{\pm} = [\cos\theta_f(N \pm \frac{f-2}{2}) \pm \sin\theta_f\,\frac{d}{d\theta_f}]\,[\frac{N\pm 1}{N}]^{\frac{1}{2}} \ . \tag{9b}$$

with the operators G and N defined by

$$(G - l - \frac{f-3}{2})\,A_{kl}^{(f)} = 0 \ , \tag{10a}$$

$$(N - k - \frac{f-2}{2})\,A_{kl}^{(f)} = 0 \ . \tag{10b}$$

The operators in (9) satisfy

$$G_{\pm}A_{kl}^{(f)} = [(p \mp q)(p \pm q + 1)]^{\frac{1}{2}}\,A_{k\,l\pm 1}^{(f)} \tag{11a}$$

$$N_{\pm} A_{kl}^{(f)} = \left[(n \mp b)(n \pm b \pm 1\right]^{\frac{1}{2}} A_{k\pm 1\ l}^{(f)} , \tag{11b}$$

with

$$\left.\begin{array}{ll} q = l + \dfrac{f-3}{2}, & b = q - \tfrac{1}{2} , \\ n = k + \dfrac{f-2}{2}, & p = n - \tfrac{1}{2} . \end{array}\right\} \tag{11c}$$

Note that

$$G_{+} A_{kk}^{(f)} = 0 , \tag{12}$$

and

$$N_{-} A_{ll}^{(f)} = 0 , \tag{13}$$

but that N_+ can increase the value of k without bound. In addition, functions $A_{kl}^{(f)}$ with $l < 0$ may be generated with repeated use of G.

In order to establish the connection of the ladder operators with a Lie algebra we cbtain from (10) and (11) the following commutation relations on the $A_{kl}^{(f)}$:

$$[G, G_{\pm}] = \pm G_{\pm} \tag{14a}$$

$$[G_{+}, G_{-}] = 2G \tag{14b}$$

and

$$[N, N_{\pm}] = \pm N_{\pm} \tag{15a}$$

$$[N_{+}, N_{-}] = -2N . \tag{15b}$$

The relations in (14) and (15) are isomorphic to those of the Lie algebras of $O(3)$ and $O(2,1)$ respectively.

Additional ladder operators may be obtained from the commutation relations of the generators $\{G, G_{\pm}, N, N_{\pm}\}_{(f)}$ and it is easily seen (cf. the results of section II for $f = 3$) that the $A_{kl}^{(f)}$ are a basis for a representation of a Lie algebra locally isomorphic to $O(3,2)$. The product space of functions

$$Z^{(f)} = A_{k_f l_f}^{(f)} A_{k_{f-1} l_{f-1}}^{(f-1)} \cdots Y_{k_3}^{(3)} \tag{16}$$

is then a basis for a representation of

$$S^{(f)} \equiv O(3,2) \otimes O(3,2) \otimes \ldots \qquad (f-2 \text{ times}), \tag{17}$$

and the generators of $O(f)$ on the f-dimensional spherical harmonics are accordingly elements of the enveloping algebra of $S^{(f)}$, restricted to the $Y_{l_f}^{(f)}$ subspace of $Z^{(f)}$.

We turn now from these general considerations of the f-dimensional spherical harmonics to the construction of the generators of the "angular" $O(f, 2)$.

II. THE ANGULAR $O(f, 2)$

We define the $2f$ operators $N_{\pm}^{(k)}$ acting on the $Y_{l_f}^{(f)}$ by

$$N_{\pm}^{(k)} = \left[\frac{x_k}{r}(a_{\pm} \pm i(\mathbf{r}\cdot\mathbf{p})) \mp irp_k\right]\left[\frac{N \pm 1}{N}\right]^{\frac{1}{2}}, \tag{20}$$

with $k = 1, 2, \ldots, f$ and

$$a_{\pm} = N \pm \frac{f-2}{2} . \tag{21}$$

The $N_{\pm}^{(k)}$ are a generalization of the $N_{\pm}$ in (9b), with $N_{\pm}^{(f)} = N_{\pm}$ in hyperspherical coordinates.

The operators N and $N_{\pm}^{(k)}$ together with the L_{jk} of (1) are a set of $(f+1)(f+2)/2$ operators with the following commutation relations:

$$[L_{jk}, L_{km}] = -iL_{jm} \tag{22a}$$

$$[L_{jk}, N_{\pm}^{(k)}] = -iN_{\pm}^{(j)} \tag{22b}$$

$$[N, L_{jk}] = 0 \tag{22c}$$

$$[N, N_{\pm}^{(k)}] = \pm N_{\pm}^{(k)} \tag{22d}$$

$$[N_{\pm}^{(j)}, N_{\pm}^{(k)}] = 0 \tag{22e}$$

$$[N_{\pm}^{(j)}, N_{\mp}^{(k)}] = -2iL_{jk} \mp 2N\delta_{jk} . \tag{22f}$$

If we define the generators $M_{ab} = -M_{ba}$ such that

$$L_{jk} = M_{jk}, \quad (j, k = 1, 2, \ldots, f) \tag{23a}$$

$$N = M_{f+1\ f+2} \tag{23b}$$

$$N_{\pm}^{(k)} = M_{f+1\ k} \pm iM_{k\ f+2} \quad , \tag{23c}$$

then the corresponding commutation relations are

$$[M_{jk}, M_{lm}] = i(g_{kl}M_{jm} + g_{jm}M_{kl} - g_{jl}M_{km} - g_{km}M_{jl}) , \tag{24a}$$

with

$$\left.\begin{aligned} g_{ab} &= 0, \text{ if } a = b \\ g_{aa} &= +1, \text{ if } a > f \\ g_{aa} &= -1, \text{ if } a \leqslant f . \end{aligned}\right\} \tag{24b}$$

Eq. (24) is sufficient to establish that the M_{jk} generate a Lie algebra locally isomorphic to the $O(f,2)$ algebra. Note that our development has implicitly included an $O(f,1)$ description of the spherical harmonics since $O(f,2) \supset O(f,1)$.

If instead of the spherical harmonics we consider functions of the type $R(r) Y_{l_f}^{(f)}$, then the full significance of the term "angular" $O(f,2)$ becomes apparent since

$$M_{jk} \left[R(r) Y_{l_f}^{(f)} \right] = R(r) \left[M_{jk} Y_{l_f}^{(f)} \right] .$$

III. THE CASE $f = 2$

The "spherical harmonics" in the two-dimensional space are the functions $A_m = (2\pi)^{-\frac{1}{2}} e^{im\phi}$ defined on the interval $0 \leqslant \phi \leqslant 2\pi$, with $m = 0, \pm 1, \pm 2, \ldots$. They are orthonormal,

$$\int_0^{2\pi} A_m^* A_{m'} \, d\phi = \delta_{mm'} , \tag{25}$$

and are the eigenfunctions of the angular momentum operator $L_{12} = -i \dfrac{d}{d\phi}$. We define the additional operators

$$J = L_{12} + h , \qquad \left(-\tfrac{1}{2} < h \leqslant \tfrac{1}{2} \right) \tag{26a}$$

$$J_\pm = e^{\pm i\phi} \left(J \pm \tfrac{1}{2} \pm is \right) , \qquad s \in R \tag{26b}$$

which have commutation relations isomorphic to those of $O(2,1)$:

$$[J, J_\pm] = \pm J_\pm \tag{27a}$$

$$[J_+, J_-] = -2J . \tag{27b}$$

The Casimir invariant $Q = J(J-1) - J_+ J_-$ has the value $w(w+1)$, with $w = -\frac{1}{2} - is$. Inspection of the generators show that the representations are unitary. The irreducible representations[21] obtained are the principal series $\mathcal{D}_P(Q, h)$ except when $h = \frac{1}{2}$ and $s = 0$. In this case the representation splits into a positive discrete series $\mathcal{D}^{+}(-\frac{1}{2})$ with $m \geqslant 0$, and a negative discrete series $\mathcal{D}^{-}(-\frac{1}{2})$ with $m \leqslant -1$.

IV. THE NONRELATIVISTIC KEPLER PROBLEM IN f-DIMENSIONS

Consider the Hamiltonian

$$H = p^2 - \frac{2}{r} \tag{28}$$

where

$$p^2 = \sum_{k=1}^{f} p_k^2, \qquad r = \left(\sum_{k=1}^{f} x_k^2\right)^{\frac{1}{2}} . \tag{29}$$

The bound state eigenfunctions of H in momentum space are related to the $(f+1)$-dimensional spherical harmonics[22, 23], and in the Schrödinger representation the generators of the $O(f+1)$ algebra which commute with H are the orbital angular momentum operators L_{jk} and the Runge-Lenz operators

$$A_k = \left[\frac{x_k}{r} - \left(\frac{f-1}{2}\right) i p_k + \sum_{j=1}^{f} L_{jk} p_j\right] [-2H]^{-\frac{1}{2}} , \tag{30}$$

with $k = 1, 2, \ldots, f$. The $O(f+1)$ Casimir invariant (cf. eq. (2)) is given by

$$L^2 + A^2 = (-2H)^{-1} - \left(\frac{f-1}{2}\right)^2 \tag{31a}$$

$$= k(k + f - 1) , \tag{31b}$$

and thus the energy eigenvalues are given by

$$E_k = -\left(k + \frac{f-1}{2}\right)^{-2}, \qquad k = 0, 1, \ldots \quad . \tag{32}$$

The results of section II indicate that a more complete group description is given by $O(f+1,2)$. In order to give a representation of the generators, we note from (22) that it is sufficient to represent the operators $N_{\pm}$ on the space of radial functions R_{kl} instead of the functions $A_{kl}^{(f+1)}$ as in (9). The corresponding representation of $N_{\pm}$ is

$$N_{\pm} = D_{N/(N\pm 1)}\left(\pm r\frac{d}{dr} - \frac{r}{N} + N \pm \frac{f-1}{2}\right)\left(\frac{N}{N\pm 1}\right)^{\frac{f+1}{2}} \qquad (33)$$

The dilatation operator is D_a, $D_a f(r) = f(ar)$. The matrix elements are

$$NR_{kl} = nR_{kl} \qquad (34a)$$

$$N_{\pm}R_{kl} = [(n\mp b)(n\pm b\pm 1)]^{\frac{1}{2}} R_{k\pm 1\ l} , \qquad (34b)$$

with $n = k + \frac{f-1}{2}$ and $b = l + \frac{f-3}{2}$. The normalization is such that

$$\int_0^\infty R_{kl}R_{k'l}r^{f-1}dr = \delta_{kk'} . \qquad (35)$$

As noted in the introduction, the use of $O(4,2)$ as a dynamical group for the Kepler problem in three dimensions is well documented. The point of interest in the present paper is that this result may be obtained from our general considerations of the spherical harmonics in f dimensions.

The similarity of the R_{kl} and the $A_{kl}^{(f+1)}$ suggests that the R_{kl} are a basis for a representation of $O(3,2)$ just as the $A_{kl}^{(f+1)}$ were seen to be in section I. We have investigated this "radial" $O(3,2)$ algebra for the case $f=3$ in a previous study[5] of the hydrogenic radial functions. The interesting feature of it is that the irreducible representations of the "radial" $O(3)$ subalgebra are characterized by half-integer eigenvalues, in contrast to the present work in which we are concerned with orbital angular momentum only.

V. THE DIPOLE OPERATOR IN $O(f,2)$

The coordinates x_j ($j = 1,2,\ldots,f$) are the components of a vector operator in the f-dimensional space, and the angular matrix elements of the x_j are simplified with the use of the Wigner–Eckart theorem for $O(f)$. The $N_\pm^{(k)}$ in (20) are also components of vector operators, and a simple rearrangement gives

$$x_k = \frac{r}{2}\left\{N_+^{(k)}\,[N(N+1)]^{-\frac{1}{2}} + N_-^{(k)}\,[N(N-1)]^{-\frac{1}{2}}\right\} . \tag{36}$$

Thus the familiar angular matrix elements of the dipole operator may be obtained directly from the "angular" $O(f,2)$ algebra. In addition, since

$$\sum_{k=1}^{f}\left(\frac{x_k}{r}\right)^2 = 1 , \tag{37}$$

substitution of (36) into (37) gives an interesting representation of the identity operator in terms of the operators $N_\pm^{(k)}$ and N.

VI. DISCUSSION

The application of the concept of a non-invariance group to problems of chemical interest represents a challenge to the theoretical chemist since precise techniques of useful application have been virtually unexplored. While the spherical harmonics in f-dimension are of interest in their own right, we have used them to indicate the usefulness of the non-invariance group for an exactly soluble problem. Such investigations are useful since they can be instructive when determining the exact or approximate invariance groups which are relevant to such diverse areas as rotation-vibration spectra, Rydberg series and configurational mixing in atoms and molecules, and the interaction of discrete states with continuum states.

One interesting area of possible application is the use of multidimensional rotation groups in the description of many-body collisions[24]. In particular we note the work of Macek[25] who demonstrated the approximate separability of the Helium atom wavefunctions in the hyperspherical coordinates $R = (r_1^2 + r_2^2)^{\frac{1}{2}}$, $\alpha = \arctan(r_1/r_2)$, $\theta_1, \theta_2, \phi_1, \phi_2$. Thus, investigation of the relevant angular properties of the wavefunctions should lead to an approximate group theoretical classification of atomic states.

The difficulty of finding useful methods of application should not be underestimated, however. In fact the determination of a *useful* non-invariance group for a simple molecular system such as H_2^+ is still an unsolved problem.

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RESUMEN

Se presenta el concepto de un grupo no-invariante, construyendo una representación del álgebra de Lie del grupo no-compacto $O(f,2)$ en los armónicos esféricos de f-dimensiones. Se hacen aplicaciones de este análisis al problema de Kepler de estados ligados en f-1 dimensiones, construyendo la parte angular del operador dipolar con los generadores del algebra $O(f,2)$. Se discuten los usos en química de grupos no-invariantes.