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1988 J. Phys. A: Math. Gen. 21 L573

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LETTER TO THE EDITOR

SO(4) group generators for k -ordered atomic systems

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Received 31 March 1988

Abstract. For atoms whose valence states obey $k = n + l$ ordering, we assume a Hamiltonian $H = H^{(k)} + H^{(l)}$, where the first term has invariance group SO(4) and is perturbed by the second. We derive matrix representations of operators which, with angular momentum, are constants of the motion and generate such an SO(4) group.

Sternheimer (1977a, b, 1979a, b) has demonstrated the usefulness of the Madelung (1936) quantum number $k = n + l$ (n is the principal quantum number and l the orbital angular momentum quantum number) in describing the ordering of excitation energy states of the s or p valence electron in 42 atomic spectra including the neutral alkali metals Na, K, Rb and Cs (Li obeys 'hydrogenic' ordering, i.e. according to the quantum number n), the singly-ionised alkaline earths Mg II, Ca II, Sr II, Ba II and Ra II, as well as Ca, Zn, Ga, Ge II, Sr, In, In II, Sn II, Tl and Pb II. The features of the spectra are that, after averaging over j values, one observes in the spectra (i) sets of levels where neighbouring k values do not overlap provided l is below some critical value, and the ionicity of the atom is not too large and (ii) within each k 'supershell' the ordering of energies is in accordance with a distinctive sequence of l values, the sequence remaining more or less the same for all k bands throughout the individual atomic spectrum. There are also remarkable similarities between these ' l patterns' from element to element.

In this letter we follow Sternheimer's scheme in which there is an assumed initial Hamiltonian with energy levels ordered by k and states which are degenerate with respect to those energies. The degeneracy is then broken by an l -dependent perturbation in the Hamiltonian. By assuming an SO(4) invariance group of such k -dependent Hamiltonians, and angular momentum to be one of the constants of the motion, we shall derive matrix representations of an operator which is the additional constant of the motion for SO(4)-invariant quantum mechanical systems where the spectrum is k ordered. This operator is thus relevant to the specific atomic systems in question.

The effective Hamiltonian can be written as the sum $H^{(k)} + H^{(l)}$. The first term, which we call the 'Madelung' Hamiltonian, will have eigenvalues which are a function of k . The second term is the perturbation. We shall consider only the unperturbed Hamiltonian, denoted $H = H^{(k)}$, which is effectively a 'single-particle' Hamiltonian‡

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‡ Thus it is expressible in the form

$$H = \frac{p^2}{2\mu} + U(r, p_j).$$

U describes the average potential in which the valence electron moves.

as we are dealing with the motion of the valence electron in the environment of the atomic core and nucleus of the atom. We shall assume the Madelung Hamiltonian acts on a 'hydrogen-like' representation space of states of the group $SO(4, 2)$ (Wybourne 1974), the states labelled by the quantum numbers (n, l, m) . These are still acceptable quantum labels despite the k ordering as $K = N + L$, in the sense of operators, commutes with L, L_3 and N . Nor is it inconsistent with the actual observed spectra to take $SO(4)$ to be the underlying symmetry of the 'primitive' k levels because *a priori* it has seemed reasonable to classifiers of atomic spectra (splittings due to, for example, spin-orbital interactions aside) to use the hydrogenic labels n, l and m as ordering numbers for these more complex spectra. Moreover we may assume angular momentum conservation (for a single electron in some potential this is not unreasonable); hence the Hamiltonian is $SO(3)$ invariant. From the assumed $SO(4)$ symmetry there is an additional conserved quantity in the problem, analogous to the Runge-Lenz vector in the Kepler problem (Goldstein 1980, Kaplan 1986). We shall call such quantities pseudo Runge-Lenz vectors (PRLV).

We consider the following ladder operators of angular momentum which are found as terms in the components of the normalised Runge-Lenz vector (Biedenharn and Louck 1981):

$$A_1^+ |nlm\rangle = -\frac{1}{2} \left(\frac{(n+l+1)(n-l-1)(l+m+1)(l+m+2)}{(2l+1)(2l+3)} \right)^{1/2} |nl+1 m+1\rangle \\ + \frac{1}{2} \left(\frac{(n+l+1)(n-l-1)(l-m+1)(l-m+2)}{(2l+1)(2l+3)} \right)^{1/2} |nl+1 m-1\rangle \quad (1)$$

$$A_2^+ |nlm\rangle = \frac{i}{2} \left(\frac{(n+l+1)(n-l-1)(l+m+1)(l+m+2)}{(2l+1)(2l+3)} \right)^{1/2} |nl+1 m+1\rangle \\ + \frac{i}{2} \left(\frac{(n+l+1)(n-l-1)(l-m+1)(l-m+2)}{(2l+1)(2l+3)} \right)^{1/2} |nl+1 m-1\rangle \quad (2)$$

$$A_3^+ |nlm\rangle = \left(\frac{(n+l+1)(n-l-1)(l+m+1)(l-m+1)}{(2l+1)(2l+3)} \right)^{1/2} |nl+1 m\rangle \quad (3)$$

$$A_i^- = (A_i^+)^{\dagger}. \quad (4)$$

These are *bona fide* vector operators and can be more rigorously derived from the characteristic identities of $SO(3)$ (Bracken and Green 1971). They specifically arise as a property of the group and are thus applicable independently of the specific quantum mechanical system in question (hydrogen or otherwise). From these we construct a class of PRLV which commute with Hamiltonians whose eigenvalues are k dependent:

$$\tilde{A}' \equiv \alpha(N, L)N_+A^- + \beta(N, L)N_-A^+. \quad (5)$$

N_{\pm} are ladder operators of n , and α and β are, at this stage, arbitrary functions of the operators N and L having eigenvalues n and l respectively on states labelled by (n, l, m) . These functions distinguish between the specific members of the class. Most significantly, by its generality, the class will include the physical PRLV for k -ordered atomic systems. Taking the conventional n -laddering operators of $SO(4, 2)$, the hydrogen dynamical group (Wybourne 1974), and requiring the PRLV to be Hermitian, gives a relationship between the two functions

$$\beta(n, l) = \alpha(n+1, l-1) \frac{(n+l)}{[(n+l+1)(n-l+1)]^{1/2}}. \quad (6)$$

In terms of ladder operators of the azimuthal quantum number, m , we obtain by incorporating (1)–(4) and (6) into the definition (5)

$$\begin{aligned}\tilde{A}'_+|nlm\rangle &= \frac{i}{2}\alpha(n+1, l-1)(n+l) \\ &\times \left(\frac{(n-l)(n-l+1)(l-m)(l-m-1)}{(2l-1)(2l+1)} \right)^{1/2} |n+1\ l-1\ m+1\rangle \\ &+ \frac{i}{2}\alpha(n, l)(n+l) \left(\frac{(n-l-1)(n-l-2)(l+m+1)(l+m+2)}{(2l+1)(2l+3)} \right)^{1/2} \\ &\times |n-1\ l+1\ m+1\rangle\end{aligned}\quad (7)$$

$$\begin{aligned}\tilde{A}'_-|nlm\rangle &= \frac{i}{2}\alpha(n+1, l-1)(n+l) \\ &\times \left(\frac{(n-l)(n-l+1)(l+m)(l+m-1)}{(2l-1)(2l+1)} \right)^{1/2} |n+1\ l-1\ m-1\rangle \\ &- \frac{i}{2}\alpha(n, l)(n+l) \left(\frac{(n-l-1)(n-l-2)(l-m+1)(l-m+2)}{(2l+1)(2l+3)} \right)^{1/2} \\ &\times |n-1\ l+1\ m-1\rangle\end{aligned}\quad (8)$$

$$\begin{aligned}\tilde{A}'_3|nlm\rangle &= \frac{i}{2}\alpha(n+1, l-1)(n+l) \left(\frac{(n-l)(n-l+1)(l+m)(l-m)}{(2l-1)(2l+1)} \right)^{1/2} |n+1\ l-1\ m\rangle \\ &+ \frac{i}{2}\alpha(n, l)(n+l) \left(\frac{(n-l-1)(n-l-2)(l+m+1)(l-m+1)}{(2l+1)(2l+3)} \right)^{1/2} \\ &\times |n-1\ l+1\ m\rangle\end{aligned}\quad (9)$$

where

$$\tilde{A}'_1 = \frac{1}{2}(\tilde{A}'_+ + \tilde{A}'_-) \quad \tilde{A}'_2 = \frac{1}{2i}(\tilde{A}'_+ - \tilde{A}'_-).\quad (10)$$

These can be shown to obey the commutation relations

$$[L_i, \tilde{A}'_j] = i\varepsilon_{ijk}\tilde{A}'_k\quad (11)$$

$$[\tilde{A}'_i, \tilde{A}'_j] = i\varepsilon_{ijk}HL_k\quad (12)$$

where L is the usual angular momentum operator and the scalar operator H has eigenstates $|nlm\rangle$ with eigenvalues

$$\frac{(n+l)^2}{4(2l+1)} [\alpha^2(n, l)(n-l-1)(n-l-2) - \alpha^2(n+1, l-1)(n-l+1)(n-l)]\quad (13)$$

which we denote by h_{nl} . In the final analysis (13) must be a function of k only. This quantity is interpreted as the eigenvalue of the desired energy operator. Equation (12) is not yet the correct SO(4) commutation relation, H having to be removed by suitable normalisation of the PRLV. We first impose the further constraint that the SO(4) Casimir invariants (Wybourne 1974) $L \cdot \tilde{A}$ and $L^2 + \tilde{A}^2$, where \tilde{A} is the normalised PRLV, must

also be k dependent. Thus the components of L and \tilde{A} are infinitesimal generators of the SO(4) group. The first Casimir is simply zero and the second has eigenvalues

$$\frac{l(l+2)X_{n+1}l-1 - (l-1)(l+1)X_{nl}}{X_{n+1}l-1 - X_{nl}} \quad (14)$$

where

$$X_{nl} \equiv \alpha^2(n, l)(n-l-1)(n-l-2). \quad (15)$$

To make the k dependence explicit denote (14) by the function $C(k)$ and let

$$h_{nl} = \frac{(n+l)^2}{4} \Phi(k) \quad \zeta(k, l) = [C(k) - (l-1)(l+1)]^{1/2}. \quad (16)$$

Thus the most general form of the arbitrary function α is given in terms of the energy function and the eigenvalues of the Casimir

$$\alpha(n, l) = \Phi^{1/2}(k) \left(\frac{C(k) - l(l+2)}{(n-l-1)(n-l-2)} \right)^{1/2}. \quad (17)$$

Substituting expressions (16) into (7)-(9) and dividing through by the square root of h_{nl} gives for the correct matrix representations of the additional SO(4) generators:

$$\begin{aligned} \tilde{A}_+ |nlm\rangle &= i\zeta(k, l) \left(\frac{(l-m)(l-m-1)}{(2l-1)(2l+1)} \right)^{1/2} |n+1 \ l-1 \ m+1\rangle \\ &+ i\zeta(k, l+1) \left(\frac{(l+m+1)(l+m+2)}{(2l+1)(2l+3)} \right)^{1/2} |n-1 \ l+1 \ m+1\rangle \end{aligned} \quad (18)$$

$$\begin{aligned} \tilde{A}_- |nlm\rangle &= -i\zeta(k, l) \left(\frac{(l+m)(l+m-1)}{(2l-1)(2l+1)} \right)^{1/2} |n+1 \ l-1 \ m-1\rangle \\ &- i\zeta(k, l+1) \left(\frac{(l-m+1)(l-m+2)}{(2l+1)(2l+3)} \right)^{1/2} |n-1 \ l+1 \ m-1\rangle \end{aligned} \quad (19)$$

$$\begin{aligned} \tilde{A}_3 |nlm\rangle &= i\zeta(k, l) \left(\frac{(l+m)(l-m)}{(2l-1)(2l+1)} \right)^{1/2} |n+1 \ l-1 \ m\rangle \\ &- i\zeta(k, l+1) \left(\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)} \right)^{1/2} |n-1 \ l+1 \ m\rangle. \end{aligned} \quad (20)$$

We derive the eigenvalues of the Casimir by complete analogy with hydrogenic atoms. We form generators of the Lie algebra of the group SU(2) × SU(2), locally isomorphic to SO(4) (Wybourne 1974), by

$$\tilde{J} = \frac{1}{2}(L + \tilde{A}) \quad \tilde{J}' = \frac{1}{2}(L - \tilde{A}) \quad (21)$$

the components satisfying

$$[\tilde{J}_i, \tilde{J}_j] = i\epsilon_{ijk}\tilde{J}_k \quad [\tilde{J}'_i, \tilde{J}'_j] = i\epsilon_{ijk}\tilde{J}'_k \quad [\tilde{J}_i, \tilde{J}'_j] = 0. \quad (22)$$

The Casimir operators of SO(4) may be written in terms of those of SU(2) (which are \tilde{J}^2 and \tilde{J}'^2 having eigenvalues $\tilde{j}(\tilde{j}+1)$ and $\tilde{j}'(\tilde{j}'+1)$ respectively where $\tilde{j}, \tilde{j}' = 0, \frac{1}{2}, 1, \dots$):

$$F = \tilde{J}^2 + \tilde{J}'^2 = \frac{1}{2}(L^2 + \tilde{A}^2) \quad (23)$$

$$G = \tilde{J}^2 - \tilde{J}'^2 = L \cdot \tilde{A}. \quad (24)$$

We have already seen that G is zero; thus $\tilde{J}^2 = \tilde{J}'^2$ or $\tilde{j} = \tilde{j}'$, so that $F(=C(k))$ has eigenvalues $2\tilde{j}(\tilde{j} + 1)$. Whereas for ordinary hydrogenic ordering (according to n) we have the relationship $n = 2j + 1$, in this case (k ordering) we have separate relationships between k and \tilde{j} depending upon whether k is odd or even. This is illustrated in figure 1 where the $SO(4, 2)$ space of states breaks up into two copies of $SU(2) \times SU(2)$ representation spaces corresponding to k being odd and even. For k an even number we obtain

$$\tilde{j} = \frac{1}{2}(\frac{1}{2}k - 1) \tag{25}$$

and for odd values of k

$$\tilde{j} = \frac{1}{2}[\frac{1}{2}(k + 1) - 1]. \tag{26}$$

Therefore

$$C(k) = \frac{1}{2}(\frac{1}{2}k - 1)(\frac{1}{2}k + 1) \quad k \text{ even} \tag{27}$$

$$C(k) = \frac{1}{8}(k - 1)(k + 3) \quad k \text{ odd.} \tag{28}$$

Inserting (27) and (28) into equations (18)-(20) provides, with angular momentum, a unique set of generators of the Lie algebra of the group $SO(4)$ which commute with a Hamiltonian whose eigenvalues are k dependent.

The additional knowledge of the functional form of the energy eigenvalues (e.g., via the spectra themselves) will result in an operator which is the constant of the

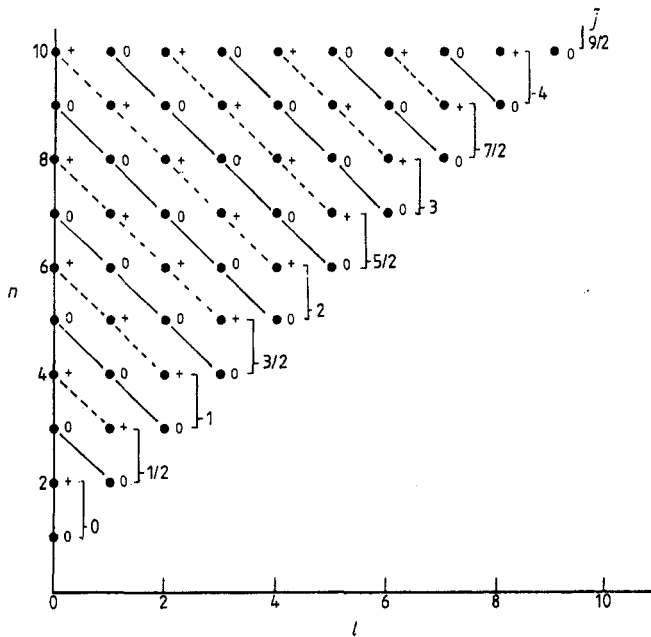


Figure 1. $SO(4, 2)$ Hilbert space of states arranged in a tower showing breakdown into two $SU(2) \times SU(2)$ representation spaces corresponding to states with $k(=n+l)$ odd (0) and even (+). The broken and unbroken lines indicate alternate $SO(4)$ representations corresponding to (degenerate) states with the same value of k . The $SU(2)$ labels, j , apply for the odd and even 'lines' of k . We see that for $j=0$, k is either 1 or 2, $j = \frac{1}{2}$ corresponds to $k=3$ or 4, $j=1$ with $k=5$ or 6, $j = \frac{3}{2}$ with $k=7$ or 8, etc. Thus we derive relations (25) and (26).

motion for quantum mechanical systems whose spectra are observed to be ordered according to the quantum number k . As such we propose that such an operator is a viable candidate for the specific constant of the motion for complex atoms consisting of a valence electron surrounding a closed electronic core such as the neutral alkali metals, where the spectrum is observed to be k ordered.

The author wishes to thank Dr P D Jarvis for suggesting the problem, and Dr J R Fox and Professor R Delbourgo for their invaluable assistance; also Dr A J Bracken (via PDJ) for comments. This work was done while at the University of Tasmania.

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