

Total State Designation for Electronic States of Periodic Systems

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The role of a complete set of commuting operators (CSCO) is first recalled with the discussion of the electronic states of two finite systems as illustrative examples. It is then shown that its role is very well transferable to sequences of finite systems that approach a real periodic system in the limit where the number of monomers becomes huge. In addition, the concept of the density of states (DOS) of total energy E , $n(E-E_0)$ (E_0 is the energy of the electronic ground state), is introduced as a system's characteristic.

1. Introduction

The state of a quantum mechanical system is completely specified by its eigenvalues associated with a complete set of commuting operators (CSCO) [1]. Consider bound states of the hydrogen atom as simple, but illustrative examples. The Hamiltonian H , the squared orbital angular momentum operator L^2 and its z -component L_z form part of the CSCO for this case (inclusion of the Runge-Lenz vector operator and of spin operators completes the CSCO). The well-known eigenvalue equations for this case can be written as (in atomic units)

$$H |nlm \ ^2L\rangle = -(2n^2)^{-1} |nlm \ ^2L\rangle, \quad L^2 |nlm \ ^2L\rangle = l(l+1) |nlm \ ^2L\rangle, \quad L_z |nlm \ ^2L\rangle = m |nlm \ ^2L\rangle, \quad (1)$$

where $|nlm \ ^2L\rangle$ denotes a state under consideration. A given set of quantum numbers $\{n, l, m\}$ ($n > 0$, $0 \leq l < n$, $-l \leq m \leq l$) identifies both the eigenvalues and the state (except for the spin part, which is, however, trivial in this case). Therefore, a state's quantum numbers can be used as labels to designate it, as has already been done in eq. (1).

Our example illustrates that “*group-theoretical deductions are usually quite easy to perform and the information so obtained concerning the solutions [of the system's Schrödinger equation (D. A.)], although not complete, often contains the essential physics*” [2]. Only the eigenvalue associated with the Hamiltonian, i.e. the energy, cannot be deduced from group theory alone. The principle just stated, and illustrated above for the hydrogen atom, holds true for periodic systems (polymers, surfaces, crystals) as well, but it is not fully exploited there. In this context, one may ask to which extent we really master the problem of electronic structure in periodic systems with the currently available software tools. Or, more provoking, to which extent are we being mastered by the limitations still present in the theories that form the basis for existing software?

In the next section, two finite systems and their low-lying electronic states are briefly discussed, as a reminder of the type of information that is contained in the symmetry labels of total electronic states and in order to introduce the density of states (DOS) of total energy E , $n(E-E_0)$ (E_0 is the energy of the electronic ground state). The subsequent section extends the discussion then to electronic states of periodic systems, in order to show how the principle stated above is applicable there.

2. Electronic states of finite systems: two examples

The first example is the oxygen atom, O, with electron configuration $1s^2 2s^2 2p^4$ (point group K_h in Schönflies notation). Three LS terms exist in Russell-Saunders coupling [2]: 3P

($L = S = 1$), 1S ($L = S = 0$), 1D ($L = 2, S = 0$). Each term has a weight $g = (2L+1)(2S+1)$, according to the number of degenerate states $|p^4 LM_L SM_S\rangle$ differing only by M_L and M_S for given L and S . It is instructive to consider the situation also under reduced symmetry, because the full rotation-reflection group K_h cannot be used with standard software tools designed for the study of electronic structure of molecules. An overview of the situation, including the cases of the finite point groups D_{2h} , C_{2v} and C_1 , is given in Table 1. It is important to remark that all properties of the states (like, e.g., degrees of degeneracy of orbital and state energies, orbital occupation numbers, orbital radial parts) are independent of the point group actually used. The density of states (DOS) of total energy E , $n(E-E_0)$, for this case is shown in Fig. 1 (up to $E-E_0 \approx 4.5$ eV, E_0 is the ground state energy).

Table 1. Low-lying electronic terms of the oxygen atom, O, and of a trinuclear transition metal complex ion, $[(\mu_3-L)M_3]^{q+}$ (assuming one unpaired electron per M ion), labeled under different point groups. See Fig. 1 for corresponding densities of states (DOS) of total energy E .

Electron configuration and point group	List of resulting electronic terms ^a
O $2p^4$:	
$(p_{+1}, p_0, p_{-1})^4$ in K_h	$^3P / ^1S / ^1D$
$(p_x, p_y, p_z)^4$ in D_{2h}	$^3B_{1g}, ^3B_{2g}, ^3B_{3g} / ^1A_g / ^1A_g(2), ^1B_{1g}, ^1B_{2g}, ^1B_{3g}$
$(p_x, p_y, p_z)^4$ in C_{2v}	$^3A_2, ^3B_1, ^3B_2 / ^1A_1 / ^1A_1(2), ^1A_2, ^1B_1, ^1B_2$
$(p_x, p_y, p_z)^4$ in C_1	$^3A(3) / ^1A / ^1A(5)$
$[(\mu_3-L)M_3]^{q+} (a,e)^3$:	
$a^2 e^1 - a^1 e^2 - e^3$ in C_3	$^2E - ^4A / ^2A, ^2A, ^2E - ^2E$
$a^2 (a,a)^1 - a^1 (a,a)^2 - (a,a)^3$ in C_1	$^2A(2) - ^4A / ^2A, ^2A, ^2A(2) - ^2A(2)$

^a Number of degenerate terms of same symmetry in parentheses.

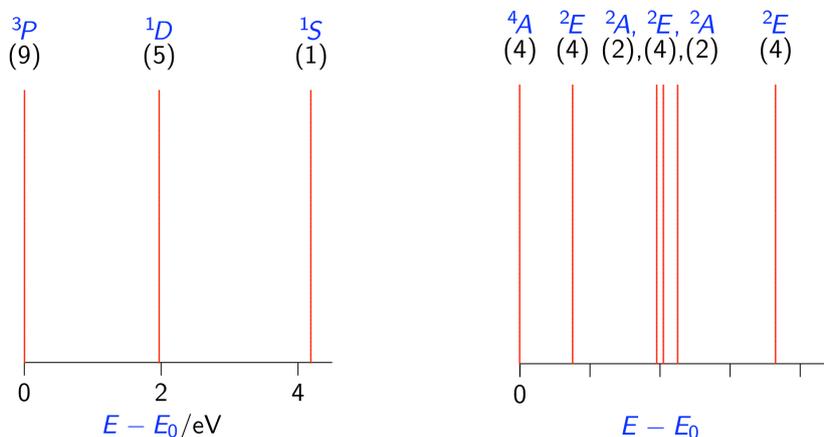


Fig. 1. Density of low-lying states (DOS) of total energy E , $n(E-E_0)$, for finite systems, being a sequence of Dirac delta “peaks” with weights (indicated in parentheses at the top of each panel). Left panel: O atom (point group K_h), DOS for LS terms [3] from electron configuration $1s^2 2s^2 2p^4$. Right panel: A trinuclear transition metal complex ion $[(\mu_3-L)M_3]^{q+}$ (point group C_3), DOS for electronic terms from electron configuration $(a,e)^3$.

Our second example is a trinuclear transition metal complex ion with a triply bridging ligand L, $[(\mu_3-L)M_3]^{q+}$ (point group C_3). We assume that each M ion contributes just a single unpaired electron, such that low-lying electronic states in ΓS coupling, $|\alpha L \gamma SM_S\rangle$, originate from an electron configuration $(a,e)^3$. The resulting sets of electronic terms, both in C_3 and in C_1 , are listed in Table 1, and a density of states (DOS) of total energy E , $n(E-E_0)$, associated

with this case is schematically shown in Fig. 1 (details of energy spacings and sequence of states are case-dependent, but unimportant for the present discussion).

The designation of a state $|I\rangle$ of a quantum mechanical system properly combines spin and space symmetry information (here denoted by a composite index I). If the state's wavefunction is constructed from single-electron functions (orbitals), then the eigenvalue associated with the Hamiltonian, the energy E_I , reduces to a linear combination of one- and two-electron integrals. For a normalized state function ($\langle I|I\rangle = 1$),

$$E_I = \langle I | \mathbf{H} | I \rangle = \sum_{ij} \gamma_{ij}^I h_{ij} + \sum_{ijkl} \Gamma_{ijkl}^I g_{ijkl}. \quad (2)$$

All summations run over orbital indices, the state-specific coefficients γ_{ij}^I and Γ_{ijkl}^I are known as structure factors or density matrix elements (for further details see [2] or any other good textbook on electronic structure theory for atoms and molecules).

3. Electronic states of periodic systems

An ideal infinite periodic system (polymer, slab, crystal) built from monomers A has an infinite number of electronic states. An important quantity of interest, irrespective of the actual electronic state of the system, is the energy per unit cell $\lim_{N \rightarrow \infty} E(A_N)/N$, which is finite (a single monomer A per unit cell was assumed). However, the limit process just indicated always ends abruptly because only finite pieces of periodic systems exist in the real world. But this implies that the tools discussed in the previous section become applicable, sometimes without great difficulties. For example, the designation $^1A_{1g}$ (point group O_h) can be given for the electronic ground state of both halite (rock salt, space group $Fm-3m$, no. 225) and diamond (space group $Fd-3m$, no. 227) crystals, if we idealize and assume cube-shaped crystals in the former case and octahedron-shaped crystals in the latter. In the case of diamond, dangling bonds at the crystal surface must have been saturated somehow (e. g. by H atoms) to make our designation valid. The situation is much more complicated for the simple metal lithium. Several polymorphs of lithium are known to exist up to moderate pressure [4], including bcc (under ambient conditions), fcc, hcp, and a low-temperature phase with samarium structure (hR9). What is the electronic ground state for each of these polymorphs, and how large are the energy differences between them at $T = 0$ K? How does the density of states (DOS) of total energy E per Li atom differ between these polymorphs? These questions cannot be answered yet.

An approach to the electronic structure of periodic systems via finite-sized structures requires again the consideration of the spin and space parts of the electronic states of these structures. The problem of designation of these states is addressed in the following.

3.1 The spin part

A set of N spins, each characterized by the same spin quantum number s ($2s = 1, 2, 3, \dots$), leads to a Hilbert space of spin functions of dimension $d = (2s + 1)^N$. The resulting total spin quantum number S can take any value from the set $\{0 \leq S_{\min}, S_{\min} + 1, \dots, S_{\max} - 1, S_{\max} = Ns\}$, and for each value of S , the associated spin projection quantum number M is restricted to $2S + 1$ values obeying the condition $-S \leq M \leq S$. Total spin states $|\alpha SM\rangle$ can then be constructed as eigenfunctions of the total spin operators \mathbf{S}^2 and \mathbf{S}_z , such that

$$\mathbf{S}^2 |\alpha SM\rangle = S(S + 1) |\alpha SM\rangle, \quad \mathbf{S}_z |\alpha SM\rangle = M |\alpha SM\rangle \quad (3)$$

(the label α distinguishes between eigenfunctions that do not differ in S and M). It is now of great interest to determine for given N the dimension of Hilbert subspaces with given M , $d(N, M)$, and with given S , $f(N, S)$. The calculation of these numbers for arbitrary s has been

solved, in principle: The dimensions $d(N, M)$ can be either read off from the expansion of their generating function $(1 + x + \dots + x^{2s})^N = \sum_k a_k x^k$ ($a_{2Ns-k} = a_k$, $d(N, M) = a_{M+N_s}$) [5] or calculated from binomial coefficients [6]. And then for $S < S_{\max}$: $f(N, S) = d(N, M = S) - d(N, M = S + 1)$ ($f(N, S_{\max}) = 1$). The numbers $f(N, S)$ satisfy an invariance condition with respect to the dimension d of the complete Hilbert space: $\sum_S (2S + 1) f(N, S) = (2s + 1)^N = d$. It is remarkable that a recursive scheme for the calculation of $d(N, M)$ has been devised already around 1800, long before the discovery of quantum mechanics and spin degrees of freedom, by L. Euler [7]. The recursive scheme for the calculation of $f(N, S)$ generalizes the well-known branching diagram for the case $s = 1/2$ [8]. For arbitrary s and given N , the maximum value of $d(N, M)$ is obtained for $|M| = S_{\min}$. The value of S for which $f(N, S)$ takes its maximum value is not known in general. But for $s = 1/2$ and given N , the maximum value of $f(N, S)$ occurs at $S_{\text{peak}} = (S_{\max}/2)^{1/2}$ (see Fig. 2), and the maximum of the weighted dimensions $(2S + 1) f(N, S)$ is at $S'_{\text{peak}} = 2^{1/2} S_{\text{peak}} = (S_{\max})^{1/2}$.

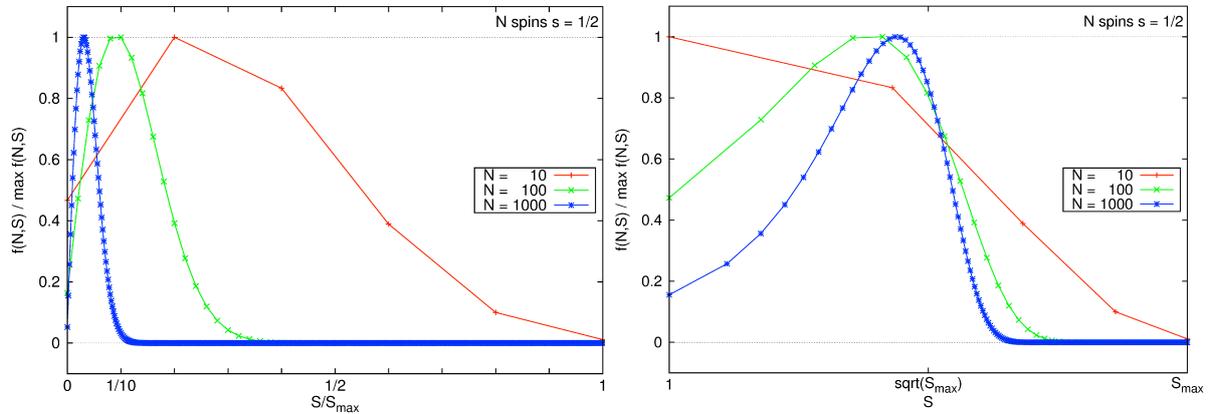


Fig. 2. Renormalized distributions of the number $f(N, S)$ of spin states with total spin S for N spins $s = 1/2$ ($0 \leq S \leq S_{\max} = N/2$, $N = 10, 100, 1000$). The maximum of $f(N, S)$ is at $S_{\text{peak}} = N^{1/2}/2 = (S_{\max}/2)^{1/2}$ for sufficiently large N . Left panel: Horizontal axis with linear scale for S/S_{\max} . Right panel: Horizontal axis with logarithmic scale for S .

3.2 Combining the spin and space parts

The combination of spin and space parts has to be done individually for every system of interest (see the examples in Sect. 2). However, a list of the possible types of electronic terms that can occur for a given sequence of systems can be straightforwardly derived from group-theoretical considerations. The following examples illustrate the situation for Li oligomers:

Li_N linear chain: Point group $D_{\infty h}$, N times $(\sigma, \rho)^1$, possible electronic terms:

$$N \text{ even: } ^{1,3,\dots}(\Sigma_g^+, \Sigma_g^-, \Sigma_u^+, \Sigma_u^-)$$

$$N \text{ odd: } ^{2,4,\dots}(\Sigma_g^+, \Sigma_g^-, \Sigma_u^+, \Sigma_u^-)$$

Li_N ring: Point group D_{nh} , N times $(s, p_l)^1$, possible electronic terms:

$$N = 2k + 1 \geq 3: ^{2,4,\dots}(A'_1, A'_2, E'_1, \dots, E'_k)$$

$$N = 2k \geq 4 \ (k = 2l): ^{1,3,\dots}(A_{1g}, A_{2g}, B_{1g}, B_{2g}, E_{1u}, E_{2g}, \dots, E_{(k-1)u})$$

$$N = 2k \geq 6 \ (k = 2l + 1): ^{1,3,\dots}(A_{1g}, A_{2g}, B_{1u}, B_{2u}, E_{1u}, E_{2g}, \dots, E_{(k-1)g})$$

Li_N planar (lozenge-shaped cutout from close-packed layer): Point group D_{2h} , N times $(s, p_x, p_y)^1$, possible electronic terms:

$$N \text{ even: } ^{1,3,\dots}(A_g, B_{1g}, B_{2u}, B_{3u})$$

$$N \text{ odd: } ^{2,4,\dots}(A_g, B_{1g}, B_{2u}, B_{3u})$$

For given N and S , the number of terms transforming according to a given irreducible representation Γ of the point group G of the system can be denoted as $f(N, S, \Gamma)$. These numbers can be calculated recursively for a given sequence of systems (e.g. linear Li_N chains, $N = 2, 3, 4$,

...). It seems to be possible to obtain recursively also all the energies E_I , eq. (2), for all possible electronic terms of given N , from the energies E_J for all possible electronic terms seen for $N-1$. In this way, a sequence of densities of states of total energy E per monomer is generated that is likely to approach the one for the periodic system in the limit $N \rightarrow \infty$.

Acknowledgments

Fruitful discussions with J. Schnack (Bielefeld University) are gratefully acknowledged.

References

- [1] Dirac P A M 1930 *The Principles of Quantum Mechanics* (Oxford : Clarendon) § 14.
- [2] Weissbluth M 1974 *Atoms and Molecules* (New York : Academic) p 204.
- [3] Kramida A, Ralchenko Yu, Reader J and NIST ASD Team 2013 *NIST Atomic Spectra Database* (version 5.0), see <http://physics.nist.gov/asd> [2014, January 19].
- [4] Guillaume C L, Gregoryanz E, Degtyareva O, McMahon M I, Hanfland M, Evans S, Guthrie M, Sinogeikin S V, Mao H-K 2011 *Nature Physics* **7** 211.
- [5] The coefficients b_k in $(x^{-s} + x^{-s+1} + \dots + x^{s-1} + x^s)^N = \sum_k b_k x^k$ generate the numbers $d(N,M)$ more directly ($d(N,M) = b_M$), but this approach requires consideration of Puiseux or Laurent polynomials (polynomials with fractional and/or negative powers), instead of just ordinary polynomials in x .
- [6] Bärwinkel K, Schmidt H-J and Schnack J 2000 *J. Magn. Magn. Mater.* **212** 240.
- [7] Euler L 1801 *Nova Acta Acad. Sci. Imper. Petropol.* **12** 47 (paper no. 709 in the Eneström index), also in Euler L (1992) *Opera Omnia* Ser 1, Vol 16 (Basel : Birkhäuser) p 28, see arXiv:math/0505425 for an English translation.
- [8] McWeeny R and Sutcliffe B T 1969 *Methods of Molecular Quantum Mechanics* (New York : Kluwer) p 67.