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Group Theoretical Approaches to Many-Body Problems in Chemistry and Physics

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Introduction

- Groups in Chemistry and Physics
- Types of Groups in Applications
- Compact and Non-Compact Groups
- Dynamical Groups
- Groups and Harmonic Oscillators
- Groups and Thermodynamic Partition Functions
- Groups and Quantum Dots
- Concluding Remarks

Groups in Chemistry and Physics

- Groups are a natural tool for exploiting symmetry in physical problems
- There are both static geometrical symmetries and dynamical symmetries
- Symmetries may be finite or continuous e.g. Compare a square with a circle
- Symmetries lead to selection rules which tell us what is not possible - not what is possible
- Via the Wigner-Eckart Theorem they lead to the calculation of matrix elements

Types of Groups in Applications

- Finite Groups 32 Point Groups, 230 Crystallographic Space Groups, Magnetic Space Groups, Black and White Groups, Permutation Groups S_n
- Finite Groups:- Finite number of group elements, representations and all representations of finite dimension
- Lie groups Infinite number of group elements and of unitary representations. Examples $SO(2)$, $SO(3)$, $SO(4)$, $SO(5)$, $SU(2)$, $SU(3)$,$SO(3,1)$, $SO(4,1)$, $SO(4,2)$ etc.
- H-atom, Harmonic oscillators, Jahn-Teller effect, Thermodynamic Partition Functions, Maxwell's Equations etc.

Compact and Non-Compact Lie Groups

- Compact Lie groups have an infinite number of finite dimensional unitary irreducible representations. cf. Rotation group $SO(3)$. Used to describe systems with a finite number of states. e.g. States of the $3d^5$ electron configuration.
- Non-compact Lie groups have an infinite number of unitary irreducible representations with the important difference - all the non-trivial unitary irreducible representations are of infinite dimension. Useful in describing systems having an infinite number of states. e.g. The complete set of discrete states of a H-atom. Representations may be discrete or continuous - may be unbounded from above, below or both.

Compact and Non-Compact Lie Groups

- In making applications we need to be able to:-
- Label representations
- Compute Group Subgroup Branching Rules
- Resolve Kronecker Products and symmetrized powers of representations
- Construct invariants and Integrity bases

Dynamical Groups

- Bohr's first paper energy levels of H-atom (in appropriate units)

$$E_n = -\frac{1}{n^2} \quad \text{with} \quad n = 1, 2, \ldots$$

  $2(n)^2$ degeneracy hidden

- Pauli notes that in a Coulombic central field for a single electron the Runge-Lenz vector leads to the higher degeneracy and the degeneracy group for the H-atom is $SU(2) \times SO(4)$

- Much later Barut and Kleinert show that all of the infinite set of discrete states of a H-atom span a single representation $H_0 = \{1(\bar{0}; 0)\}$ of a non-compact group $SO(4, 2) \sim SU(2, 2)$ that contains the orbital degeneracy group $SO(4)$ as a subgroup

Dynamical Groups

- The $SO(4)$ symmetry is broken for more than one electron
- Nevertheless, it can be useful to consider $n-$electron states constructed from symmetrized powers of $H_0 = \{1(\bar{0};0)\}$
- Using the theory of symmetric functions it has been possible to develop algorithms for resolving symmetrized powers and branching rules for both compact and non-compact Lie groups
- $$H_0 \otimes \{2\} = \sum_{k \geq 0}^{\infty} \{2(\overline{2k};2k)\} \quad (S=0)$$
$$H_0 \otimes \{1^2\} = \sum_{k \geq 0}^{\infty} \{2(\overline{2k+1};2k+1)\} \quad (S=1)$$
- Knowing the relevant $U(2,2)$ irreps is a significant first step

Groups and Harmonic Oscillators

- The energy levels of a $d-$dimensional isotropic harmonic oscillator are given by

$$E_n = (n + \frac{d}{2}) \quad \text{with} \quad n = 0, 1, 2, \ldots$$

- Each level has an orbital degeneracy,$D_d(n)$, depending on d,

$$D_1(n) = 1, \quad D_2(n) = n + 1, \quad D_3(n) = \frac{(n+)(n+2)}{2}, \ldots$$

- The orbital degeneracy group of an isotropic $d-$dimensional harmonic oscillator is $U(d)$ with the degenerate states spanning the symmetric representations $\{n\}$

- The *even* parity states have n *even* and the *odd* parity n *odd*

Groups and Harmonic Oscillators

- For $N-$noninteracting particles in d dimensions the dynamical group is the metaplectic group $Mp(2Nd)$. The infinite set of states span the fundamental representation $\tilde{\Delta}$. Under

$$Mp(2Nd) \to Sp(2Nd, \Re) \quad \tilde{\Delta} \to \Delta_+ + \Delta_-$$

where $\Delta_\pm$ are the two basic irreps of $Sp(2Nd, \Re)$ with D_+ contains all the states of even parity and Δ_- those of odd parity

- $Sp(2Nd, \Re)$ has a rich subgroup structure. e.g.

$$Sp(2Nd, \Re) \supset Sp(2d, \Re) \times O(N) \supset U(d) \times S(N) \supset O(d) \times S(N)$$

- With spin the complete dynamical group is $SU(2) \times Mp(2Nd)$ and the degeneracy group is $SU(2) \times U(d)$

Groups and Harmonic Oscillators

- Before one can attempt practical applications one must develop appropriate algorithms for handling both compact and non-compact Lie groups
- Methods for computing all the relevant branching rules, Kronecker products, symmetrized powers have been developed
- Basic to the whole programme has been the development of algorithms for calculating group properties in terms of the combinatorial properties of symmetric functions
- Detailed examples of the enumeration of states for 12 particles have been given elsewhere

Applications for harmonic oscillator many-body systems

- The symplectic model of nuclei has been extensively studied and provides a natural link between shell models and collective models
- The symplectic models used for nuclei are largely transferable to problems involving many-electrons in quantum dots
- Symplectic models lead to a natural way of counting states and as such are a useful tool for computing thermodynamic partition functions for finite numbers of bosons and fermions and shed light on relationships between boson and fermion many particle systems

Thermodynamic Partition Functions for Bosons and Fermions

- The development of traps that confine a finite number of ultracold atoms in a harmonic potential requires the development of thermodynamic partition functions for a finite number N of non-interacting bosons and fermions

- $$\mathcal{Z}_N(\beta) = \mathcal{T}r\left(e^{-\beta\mathcal{H}}\right) \quad \beta = (k_B T)^{-1}$$

  with

  $$\mathcal{H} = \sum_{i=1}^{N} \mathcal{H}_i$$

  the Hamiltonian, the sum of N identical single particle Hamiltonians, with a spectrum of energy eigenvalues $\mathcal{E}_1, \mathcal{E}_2, \ldots$ (with possible degeneracies)

Thermodynamic Partition Functions for Bosons and Fermions

- For a single boson or fermion

$$\mathcal{Z}_1(\beta) = \sum_{i=1} e^{(-\beta \mathcal{E}_i)}$$

- Introduce a set of variables $(x) = (x_1, x_2, \dots)$, not necessarily finite in number with $x_i = e^{(-\beta \mathcal{E}_i)}$.

- Using the properties of symmetric functions we obtain

$$\mathcal{Z}_N(\beta)^{\pm} = \sum_{|\sigma|=N} \varepsilon_\sigma^{\pm} z_\sigma^{-1} \mathcal{Z}_1(\sigma\beta)$$

where $\varepsilon^+ = 1, \varepsilon^- = (-1)^{|\sigma|-\ell(\sigma)}$ and $z_\sigma = \prod_{i\geq 1} i^{m_i} m_i!$

Thermodynamic Partition Functions for Bosons and Fermions

- Thus the canonical partition function for N-noninteracting bosons or fermions is completely determined by the single particle partition function. The coefficients sum to unity for bosons $(+)$ and to zero for fermions $(-)$. For example:-

$$\mathcal{Z}_5(\beta)^{\pm} = \frac{1}{120}\big(24\mathcal{Z}_1(5\beta) \pm 30\mathcal{Z}_1(4\beta)\mathcal{Z}_1(\beta) \pm 20\mathcal{Z}_1(3\beta)\mathcal{Z}_1(2\beta)$$
$$+20\mathcal{Z}_1(3\beta)\mathcal{Z}_1(\beta)^2 + 15\mathcal{Z}_1(2\beta)^2\mathcal{Z}_1(\beta) \pm 10\mathcal{Z}_1(2\beta)\mathcal{Z}_1(\beta)^3 + \mathcal{Z}_1(\beta)^5\big)$$

However, this assumes a single spin state. For fermions of spin $s = \frac{1}{2}$ the partition function is appropriate to five such fermions with maximal spin projection $M_S = \frac{5}{2}$. The complete partition function $\mathcal{Z}_5^T$ covering the complete set of spin states can be constructed to give

Thermodynamic Partition Functions for Bosons and Fermions

- $$\begin{aligned}\mathcal{Z}_5^T &= \mathcal{Z}_5^{\uparrow}(\beta) + \mathcal{Z}_4^{\uparrow}(\beta)\mathcal{Z}_1^{\downarrow}(\beta) + \mathcal{Z}_3^{\uparrow}(\beta)\mathcal{Z}_2^{\downarrow}(\beta) \\ &+ \mathcal{Z}_2^{\uparrow}(\beta)\mathcal{Z}_3^{\downarrow}(\beta) + \mathcal{Z}_1^{\uparrow}(\beta)\mathcal{Z}_4^{\downarrow}(\beta) + \mathcal{Z}_5^{\downarrow}(\beta)\end{aligned}$$

  where the $Z_n^{\uparrow}(\beta)$ indicates that the spin projection is $M_S = \frac{n}{2}$ and $Z_n^{\downarrow}(\beta)$ a spin projection $M_S = -\frac{n}{2}$. Analogous results can be constructed for other spin states of both fermions and bosons. We note the close correspondence with the $LL-$coupling of atomic physics.

Groups and Quantum Dots

- The electrons of a quantum dot are confined in an approximately parabolic potential. Close relationship with a many-electron system subject to a harmonic oscillator potential.

- $$V(r_i, r_j) = 2V_0 - \tfrac{1}{2} m^* \Omega^2 |r_i - r_j|^2$$

  m^* electron effective mass and V_0 and Ω are positive parameters

- For an $N-$electron quantum dot each with a charge $-e$, a $g-$factor g^*, spatial coordinates r_i and spin components $s_{z,i}$ along the $z-$axis with a magnetic field B along the $z-$axis the spatial part of the Hamiltonian can be written as

  $$H_{space} = \frac{1}{2m^*} \sum_i \left[p_i + \frac{eA_i}{c} \right]^2 + \tfrac{1}{2} m^* \omega_0^2 \textstyle\sum_i |r_i|^2 + \sum_{i<j} V(r_i, r_j)$$

Groups and Quantum Dots

- and the spin part as

$$H_{spin} = -g^* \mu_B B \sum_i s_{z,i}$$

- The momentum and vector potential associated with the $i-th$ electron

$$p_i = (p_{x,i}, p_{i,y}) \quad A_i = (A_{x,i}, A_{y,i})$$

For a circular gauge $A_i = B(-y_i/2, x_i/2, 0)$ we have

$$\begin{aligned} H_{space} &= \tfrac{1}{2m^*} \textstyle\sum_i p_i^2 + \tfrac{1}{2} m^* \omega_0^2(B) \textstyle\sum_i |r_i|^2 \\ &+ \textstyle\sum_{i<j} \left[2V_0 - \tfrac{1}{2} m^* \Omega^2 |r_i, r_j|^2\right] \tfrac{\omega_c}{2} \textstyle\sum_i L_{z,i} \end{aligned}$$

where $\omega_0(B) = \omega_0^2 + \omega_c^2/4$ and $\omega_c = eB/m^*c$.

Groups and Quantum Dots

- The dynamical algebra for a mesoscopic $N-$electron system in d dimensions (usually $d = 1, 2$) is the non-compact Lie group $Sp(2Nd, \Re)$
- Subalgebras of $Sp(2Nd, \Re)$ formed by subsets of the defining generators that close under commutation. For example

$$\begin{aligned} Sp(2Nd, \Re) \quad &\supset Sp(2, \Re) \times O(Nd) \supset Sp(2, \Re) \times O(N) \times O(d) \\ &\supset U(1) \times O(N) \times O(d) \end{aligned}$$

Note the separation of the spatial $O(d)$ and particle $O(N)$ dependencies

Groups and Quantum Dots

- The Hamiltonian may be written in terms of the generators of $Sp(2,\Re)$, $O(d)$ and $Sp(2N,\Re)$. Practical calculation then involves the evaluation of matrix elements of the group generators in a harmonic oscillator basis, a well-known problem in symplectic models of nuclei.
- For further details see:

- Grudziński K and Wybourne B G, *Symplectic models of n−particle systems* Rept. Math. Phys. **38** 251 (1996)
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- King R C and Wybourne B G, J. Phys.A: Math. Gen. **18** 3113 (1985)