Symmetry and Quantum-chemical Calculations

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Announcement

- Bollocks to Brexit!

Aims

- Brief review of some relevant elementary mathematics.
- Symmetry and the Hamiltonian.
- Point group symmetry: D_{2h} and its subgroups.
- General point groups.
- Permutational symmetries.
- Some literature.

Abstract groups

- A set $\mathscr{G}$ with elements $G, H \dots$ and an operator to *combine* them as $G \circ H$. If for *all* $G, H \dots$
    - $G \circ H \in \mathscr{G}$ (closure)
    - $(G \circ H) \circ J = G \circ (H \circ J)$ (associativity)
    - Element E such that $E \circ G = G \circ E = G$ (identity)
    - $G \circ G^{-1} = G^{-1} \circ G = E$ (inverse)

  then $\mathscr{G}$ is a group.
    - If also all $G \circ H = H \circ G$ (commutativity) the group is *Abelian*.

- The *order* of the group g is the number of distinct elements G (could be infinite).

Examples of groups

- Transformations of a fixed nuclear framework (*point groups*).
  ○ is successive transformations.
- Permutations of N objects: the *symmetric group $\mathscr{S}(N)$*. ○ is successive permutations.
- The integers under addition. Must include positive and negative integers: identity element is 0. Not a group under multiplication (no inverse).
- *Cyclic groups* — generating element x with $x^g = E$ and $\mathscr{G} = \{E, x, x^2, x^3, ..., x^{g-1}\}$.
  Any cyclic group is Abelian, and if g is prime any group of order g is cyclic.

Multiplication tables

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	B	E	F	C	D
B	B	E	A	D	F	C
C	C	D	F	E	A	B
D	D	F	C	B	E	A
F	F	C	D	A	B	E

- Not cyclic, not Abelian.
- E, A, B form a *subgroup*: $\mathscr{H} \subseteq \mathscr{G}$. As do E, C, etc.
- Groups with the same multiplication table are *isomorphic*.

Abelian Group

	E	A	B	C
E	E	A	B	C
A	A	E	C	B
B	B	C	E	A
C	C	B	A	E

	E	A	B	C
Γ_1	1	1	1	1
Γ_2	1	1	-1	-1
Γ_3	1	-1	1	-1
Γ_4	1	-1	-1	1

Representations, Characters

	E	A	B	C
Γ_1	1	1	1	1
Γ_2	1	1	-1	-1
Γ_3	1	-1	1	-1
Γ_4	1	-1	-1	1

- $\sum_G \Gamma_i(G)\Gamma_j(G) = g\,\delta_{ij}$. Orthogonality
- Each Γ_i is a *representation* of the group:
  if $GH = J$, $\Gamma_i(G)\Gamma_i(H) = \Gamma_i(J)$.
- *Group characters*, typically denoted $\chi^\alpha(G)$ for $\Gamma_\alpha(G)$.
- Group representations is a more complicated subject than just characters — non-Abelian groups, matrix representations.

Symmetry and the Hamiltonian

- Exact solution: $\hat{H}\Psi = E\Psi$.
- Consider an operator $\hat{P}$ such that $\hat{P}\hat{H} = \hat{H}\hat{P}$. Then

$$
\begin{aligned}
\hat{H}\hat{P}\Psi &= \hat{P}\hat{H}\Psi \\
&= \hat{P}E\Psi \\
&= E\hat{P}\Psi
\end{aligned}
$$

- Hence $\hat{P}\Psi$ is an eigenfunction of $\hat{H}$ with the same eigenvalue E as Ψ.
- We call $\hat{P}$ a *symmetry* of the Hamiltonian and when $\hat{P}^{-1}\hat{H}\hat{P} = \hat{H}$ we say the Hamiltonian is a *totally symmetric* operator.

The Hamiltonian

- The full (non-Born-Oppenheimer!) Hamiltonian

$$\hat{H}_{\text{mol}} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{A=1}^{K}\frac{1}{2M_A}\nabla_A^2 + \sum_{i>j}r_{ij}^{-1} - \sum_{i,A}Z_A r_{iA}^{-1} + \sum_{A>B}Z_A Z_B r_{AB}^{-1}.$$

- Comprises nuclear and electronic Laplacians (isotropic) and interparticle distances (scalars). Very symmetric!
- *Arbitrary* rotations, reflections, inversion.
- Spin-independent, so spin operators commute with it.
- Invariant to permutation of identical particles.

Born-Oppenheimer Hamiltonian

- After B-O approximation

$$\hat{H} \equiv \hat{H}_{\text{elec}} = -\frac{1}{2}\sum_i \nabla_i^2 + \sum_{i>j} r_{ij}^{-1} - \sum_{i,A} Z_A r_{iA}^{-1} + \sum_{A>B} Z_A Z_B R_{AB}^{-1}.$$

- Spin-independent, so spin operators still commute with it.
- Still invariant to permutation of identical particles.
- *But* only invariant to operations that leave the nuclear framework unchanged (point groups).

D_{2h} and subgroups

- Abelian.
- For any $G \in \mathscr{G}$, $G^2 = E$.
- Easily represented in computer implementations (bit strings and logical operations).
- Focus here on C_{2v} as an example.

C_{2v} **character table**

	E	σ_{yz}	σ_{xz}	C_2^z
A_1	1	1	1	1
B_2	1	-1	1	-1
B_1	1	1	-1	-1
A_2	1	-1	-1	1

- This is not arbitrary/crazy/pointless ordering of symmetry elements and representations!
- *Mulliken convention*. Planar C_{2v} molecule sits in xz-plane. Labels based on this ordering.
- This ordering of symmetry elements was originally the form to be used with the MOLECULE integral program of Almlöf: inherited by CFOUR, Dalton, Molcas, Molpro. . .

Water exercise
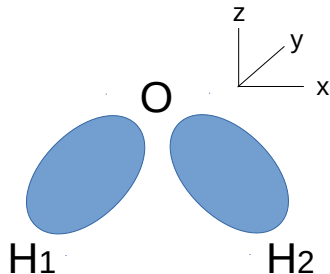
OH sp^3 hybrid bonds

Water exercise

- Orbital occupancies:

O 1s	a_1
OH bonds	$a_1 + b_2$
lone pairs	$a_1 + b_1$

- Can we do better than hand-waving to get the symmetry-adapted occupation $1a_1^2 2a_1^2 3a_1^2 1b_2^2 1b_1^2$?

- Yes! (Otherwise I wouldn't have asked...)

Projection operators

- For an arbitrary function f, the operation

$$\mathscr{P}^{\alpha} f \overset{def}{=} g^{-1} \sum_{G} \chi^{\alpha}(G) \, G f$$

  is either zero, or a function F^{α} that transforms as a *basis function* for representation α.

- $\mathscr{P}^{\alpha}$ is a projection operator.

- This means that

$$H F^{\alpha} = H \mathscr{P}^{\alpha} f = \chi^{\alpha}(H) F^{\alpha}.$$

- For example

$$\mathscr{P}^{B_2}(OH_1) = \frac{1}{2} (OH_1 - OH_2).$$

Projection operators

- We can run this in reverse. We have

$$
\begin{aligned}
b_2 &= \mathscr{P}^{B_2}(OH_1) = \frac{1}{2}(OH_1 - OH_2) \\
a_1 &= \mathscr{P}^{A_1}(OH_1) = \frac{1}{2}(OH_1 + OH_2)
\end{aligned}
$$

so $OH_1 = a_1 + b_2$ and $OH_2 = a_1 - b_2$. The "pure" representations A_1, B_2, etc., are *irreducible representations*.

- Combinations like $a_1 + b_2$ are *reducible*.

- This assumes additional significance for non-Abelian groups.

Operator symmetries

- Hartree-Fock or Kohn-Sham Fock operator: totally symmetric (so eigenfunctions — molecular orbitals — are symmetry-adapted).

- Not necessarily true for other operators: μ in C_{2v} is $A_1 + B_1 + B_2$: only the first can appear in an expectation value.

- Non-totally symmetric operators can appear in transition matrix elements, response properties, etc.

You cannot "turn off" symmetry!

- If the system has symmetry, it will appear.
- You cannot just say "the symmetry is C_1": you have to enforce it!
- E.g., distort the molecule to lower the symmetry (the molecular gradient is totally symmetric, so geometry optimizations will not break symmetry without additional input).
- Make H_2O input geometry linear, a geometry optimization will leave it linear.

Non-Abelian Groups

- For D_{2h} and its subgroups our representations were all numbers (in fact ± 1).

- Not surprising: Abelian groups and only "scalars" commute.

- These irreducible representations are "one-dimensional".

- Non-commuting quantities: irreducible representation *matrices* of higher dimension.

- E.g., for our group of order 6, isomorphic to C_{3v}, D_3, and $\mathscr{S}(3)$.

- Use NH_3: N on z-axis, H_1 and N lie in xz-plane.

Group of order 6

	E	A	B	C	D	F
	E	C_3	C_3^2	σ_v^a	σ_v^b	σ_v^c
A_1	1	1	1	1	1	1
A_2	1	1	1	-1	-1	-1
$(E)_{11}$	1	$-\frac{1}{2}$	$-\frac{1}{2}$	1	$-\frac{1}{2}$	$-\frac{1}{2}$
$(E)_{21}$	0	$\frac{\sqrt{3}}{2}$	$-\frac{\sqrt{3}}{2}$	0	$-\frac{\sqrt{3}}{2}$	$\frac{\sqrt{3}}{2}$
$(E)_{12}$	0	$-\frac{\sqrt{3}}{2}$	$\frac{\sqrt{3}}{2}$	0	$-\frac{\sqrt{3}}{2}$	$\frac{\sqrt{3}}{2}$
$(E)_{22}$	1	$-\frac{1}{2}$	$-\frac{1}{2}$	-1	$\frac{1}{2}$	$\frac{1}{2}$

Matrix representations

- Two sets of matrices for irreducible representations α and β:

$$\sum_G D_{ij}^{\alpha}(G)^* D_{kl}^{\beta}(G) = g n_{\alpha}^{-1} \delta_{\alpha\beta} \delta_{ik} \delta_{jl}.$$

Great Orthogonality Theorem. n_{α} is dimension of representation α.

- Can show, e.g.,

$$\sum_{\alpha} n_{\alpha}^2 = g.$$

- Hence two groups of order 6: $1^2 + 1^2 + 1^2 + 1^2 + 1^2 + 1^2$ (cyclic group, Abelian) and $1^2 + 1^2 + 2^2$.

- Simplify things a bit by using characters: *trace* of the representation matrices.

Group of order 6: characters

	E	C_3	C_3^2	σ_v^a	σ_v^b	σ_v^c
A_1	1	1	1	1	1	1
A_2	1	1	1	-1	-1	-1
E	2	-1	-1	0	0	0

- Still some redundancy here: some elements have the same character.
- These are in the same *class*.

Group of order 6: classes

	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	
A_2	1	1	-1		R_z
E	2	-1	0	(x,y)	(R_x, R_y)

- Common to show behaviour of Cartesian directions and rotations around axes.

Group of order 6: classes

	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	
A_2	1	1	-1		R_z
E	2	-1	0	(x,y)	$(R_x,\, R_y)$

- *Reduction* of a representation $\chi = \sum_\alpha c_\alpha \chi^\alpha$ using

$$c_\alpha = g^{-1} \sum_G \chi(G)^* \chi^\alpha(G),$$

or easier $$c_\alpha = g^{-1} \sum_K N_K \chi(G_K)^* \chi^\alpha(G_K),$$

where the sum is over *classes*, N_K number of elements in class K, and G_K is an operator from that class.

Group of order 6: classes

	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	
A_2	1	1	-1		R_z
E	2	-1	0	(x,y)	(R_x, R_y)

- Given

$$c_\alpha = g^{-1} \sum_K N_K \chi(G_K)^* \chi^\alpha(G_K),$$

easy to show $E \otimes E$ with $\chi = 4, 1, 0$ is $A_1 + A_2 + E$.

- Projection operators

$$\mathscr{P}^\alpha = g^{-1} n_\alpha \sum_G \chi^\alpha(G)^* G$$

when symmetry-adapted functions are desired.

Group of order 6: projection

	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	
A_2	1	1	-1		R_z
E	2	-1	0	(x,y)	(R_x, R_y)

- Given

$$\mathscr{P}^{\alpha} = g^{-1} n_\alpha \sum_G \chi^{\alpha}(G)^* G$$

we can e.g., obtain symmetry-adapted functions from s_1, s_2, s_3 on H's in NH_3.

Group of order 6: projection

	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	
A_2	1	1	-1		R_z
E	2	-1	0	(x,y)	(R_x, R_y)

- We obtain

$$\mathscr{P}^{A_1} s_1 = \frac{1}{3}(s_1 + s_2 + s_3)$$

$$\mathscr{P}^{A_2} s_1 = 0$$

$$\mathscr{P}^{E} s_1 = \frac{1}{6}(2s_1 - s_2 - s_3)$$

$$\mathscr{P}^{E} s_2 = \frac{1}{6}(2s_2 - s_1 - s_3)$$

Group of order 6: projection

- We obtained

$$
\begin{aligned}
\mathscr{P}^{A_1} s_1 &= \frac{1}{3}\left(s_1 + s_2 + s_3\right) \\
\mathscr{P}^{A_2} s_1 &= 0 \\
\mathscr{P}^{E} s_1 &= \frac{1}{6}\left(2s_1 - s_2 - s_3\right) \\
\mathscr{P}^{E} s_2 &= \frac{1}{6}\left(2s_2 - s_1 - s_3\right)
\end{aligned}
$$

- These two E basis functions are not orthogonal. Orthogonalization gives a function proportional to $s_2 - s_3$ for the "partner" function.

Group of order 6: projection

- Instead of character projectors we can construct projectors using full matrix irreducible representations.
- These immediately give partner functions without orthogonalization and have many other advantages.
- Downside: must have tables of full matrix representations. (See cited references at end).
- Beyond scope of today's lecture.

Spin

- Spin-independent Hamiltonian: spin is a good quantum number.
- *Spin-adapted* methods: construct spin eigenfunctions. (Let me count the ways. . .)
- Spin-projected Slater determinants, symmetric group methods, "unitary group" methods, bonded functions. . .
- For treatment of spin-dependent operators as perturbations, can work in a basis of spin eigenfunctions (e.g., singlet/triplet spin-orbit coupling).
- Full treatment with spin-dependent Hamiltonians: relativistic methods ("double groups", "ray representations").

General linear group

- Set of $n \times n$ nonsingular matrices **A** with real entries. $|A| \neq 0$.
- Binary operation: matrix multiplication. This gives the *general linear group $GL(n, \mathbb{R})$*.
- Matrix multiplication is not commutative. Explore this with a set of basis matrices $\mathbf{E}^{pq}$ with the property

$$E^{pq}_{ij} = \delta_{pi}\delta_{qj},$$

and write **A** as

$$\mathbf{A} = \sum_{pq} A_{pq} \mathbf{E}^{pq}.$$

- This is like expanding a function in some basis.
- So what about matrix multiplication? Look at the basis matrices. . .

General linear group

- Multiplication of basis matrices:

$$[\mathbf{E}^{pq}, \mathbf{E}^{rs}]_{ij} = \sum_k E^{pq}_{ik} E^{rs}_{kj} - \sum_k E^{rs}_{ik} E^{pq}_{kj}.$$

- This gives

$$
\begin{aligned}
\sum_k E^{pq}_{ik} E^{rs}_{kj} - \sum_k E^{rs}_{ik} E^{pq}_{kj} &= \sum_k \delta_{pi}\delta_{qk}\delta_{rk}\delta_{sj} - \sum_k \delta_{ri}\delta_{sk}\delta_{pk}\delta_{qj} \\
&= \delta_{qr}\delta_{pi}\delta_{sj} - \delta_{ps}\delta_{ri}\delta_{qj} \\
&= \delta_{qr}E^{ps}_{ij} - \delta_{ps}E^{rq}_{ij},
\end{aligned}
$$

General linear group

- In matrix form

$$[\mathbf{E}^{pq}, \mathbf{E}^{rs}] = \delta_{qr}\mathbf{E}^{ps} - \delta_{ps}\mathbf{E}^{rq}.$$

or

$$\mathbf{E}^{pq}\mathbf{E}^{rs} - \delta_{qr}\mathbf{E}^{ps} = \mathbf{E}^{rs}\mathbf{E}^{pq} - \delta_{ps}\mathbf{E}^{rq}.$$

- Look familiar...?

$$[E_{PQ}, E_{RS}] = \delta_{QR}E_{PS} - \delta_{PS}E_{RQ}.$$

General linear group

- This relationship between second quantization and the general linear group is arguably the most fundamental one between group theory and quantum mechanics.

- Everything useful about these *generators* of $GL(n, \mathbb{R})$ can be taken over and exploited.

- Usually referred to as the *unitary group approach*, although strictly speaking the generators of the latter would be skew-symmetric combinations $E_{PQ} - E_{QP}$.

Antisymmetry

- A configuration like $1e^1 2e^1$ in C_{3v} gives rise to singlet and triplet states from coupling two spins, and $E \otimes E$ gives $A_1 + A_2 + E$ from spatial symmetry, so we get $^1A_1, ^1A_2, ^1E, ^3A_1, ^3A_2, ^3E$.

- But for e^2 this is not consistent with antisymmetry of the wave function.

- Routinely teach this with p^2 and enumerate all the possible M_S and M_L combinations ("microstates") and after some guesswork we obtain $^3P, ^1D, ^1S$.

- How do we do this for e^2 in C_{3v}? *Not using microstates!*

Antisymmetry

- Antisymmetry results from using symmetric group projectors, specifically, apply a projector for the antisymmetric one-dimensional irreducible representation of the permutation group.

- Do this once and for all. Get

$$\chi^{S=1;\alpha}(G) = \frac{1}{2}\left([\chi^{\alpha}(G)]^2 - \chi^{\alpha}(G^2)\right)$$

$$\chi^{S=0;\alpha}(G) = \frac{1}{2}\left([\chi^{\alpha}(G)]^2 + \chi^{\alpha}(G^2)\right)$$

  for triplet and singlet respectively.

- E.g., e^2 in C_{3v} gives $^3A_2, {}^1A_1, {}^1E$.

Equivalent electrons

- Works for triply degenerate cases like t_2^2 (and for p^2...).
- Three electrons and triple-or-more degeneracy

$$\chi^{S=3/2;\alpha}(G) = \frac{1}{6}\left([\chi^{\alpha}(G)]^3 - 3\chi^{\alpha}(G^2)\chi^{\alpha}(G) + 2\chi^{\alpha}(G^3)\right)$$

$$\chi^{S=1/2;\alpha}(G) = \frac{1}{3}\left([\chi^{\alpha}(G)]^3 - \chi^{\alpha}(G^3)\right)$$

  for quartet and doublet respectively.
- E.g., t_{1u}^3 in O_h gives rise to $^4A_{1u}$, ^2E_u, $^2T_{1u}$, and $^2T_{2u}$.
- Don't guess! Recipe for disaster...

Favourites

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