Transitions in systems of identical particles and selection rules

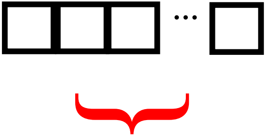
Transitions in an external (classical) field

Hamiltonian $\hat{H}_0$ of a system of n identical particles (e.g., a molecule) is invariant w.r.t.

1. permutations of both co-ordinates and spins of identical particles;
2. inversion

$$\hat{H}_0 \sim \sum_{\{\lambda\}} \left\{ \{\lambda\}_c \otimes \{\lambda\}_s \right\}_{\{n\}_{cs}} \otimes \mathfrak{g}$$

$\{ n \}$:



n boxes

Interaction operator $\hat{V}$ is a convolution of an external field (electric or magnetic field or its spatial derivatives of the kth order) operator $\hat{F}$ and the ”intrinsic” transition operator $\hat{Q}$ (a multipole moment);

$$\hat{V} = \sum_{i_0=x}^{z} \sum_{i_1=x}^{z} \cdots \sum_{i_k=x}^{z} \hat{F}_{i_0 i_1 \ldots i_k} \hat{Q}_{i_0 i_1 \ldots i_k}$$

$\hat{V}$ is invariant w.r.t. inversion:

$$\hat{F} \sim \mathfrak{g} \Leftrightarrow \hat{Q} \sim \mathfrak{g}, \qquad \hat{F} \sim \mathfrak{u} \Leftrightarrow \hat{Q} \sim \mathfrak{u}$$

$\hat{V}$ is invariant w.r.t. permutations of the identical particles $\hat{F}$ does not contain their co-ordinates/spins, therefore

$$\hat{Q} \sim \sum_{\{\mu\}} \left\{ \{\mu\}_c \otimes \{\mu\}_s \right\}_{\{n\}_{cs}}$$

Internal states of the system:

$\left|\left\{\{\lambda\}_c \otimes \{\lambda\}_s\right\}_{\{n\}_{cs}};\ P\right\rangle$ for bosons;

$\left|\left\{\{\lambda\}_c \otimes \{\tilde{\lambda}\}_s\right\}_{\{1,1,\ldots,1\}_{cs}};\ P\right\rangle$ for fermions

$P = \pm 1$ is the parity

Transitions between the initial (i) and final (f) states are allowed if

1) $\hat{Q} \sim \mathfrak{g},\ P_f = P_i$ or $\hat{Q} \sim \mathfrak{u},\ P_f = -P_i$

2) states with the permutation symmetries $\{\lambda_i\}$ and $\{\lambda_f\}$ can be coupled by an operator $\sim \{\mu\}$ contained in the expansion of $\hat{Q}$
If $\hat{Q} = \hat{Q}_c \hat{Q}_s$, where $\hat{Q}_c \sim \{n\}$ and $\hat{Q}_s \sim \{n\}$ (e.g., the interaction is spin-independent, $\hat{Q}_s = \text{const}$), then $\{\lambda_f\} = \{\lambda_i\}$
Non-trivial $\{\mu\} \neq \{n\}$ can be present in $\hat{Q}$ only for magnetic interactions (with magn.moments of particles) and in higher approximations, where the inhomogeneity of the magnetic field plays a role ($\Rightarrow$ a relatively weak process)

Collisions of molecules

Molecules #1 and #2 contain n_1 and n_2 nuclei of the same isotope, respectively

$$\hat{H}_j \sim \sum_{\{\lambda\}} \left\{ \{\lambda\}_c \otimes \{\lambda\}_s \right\}_{\{n_j\}_{cs}} \otimes \mathfrak{g}, \qquad j = 1, 2$$

Interaction operator

$$\hat{W} \sim \sum_{\{\mu\}} \left\{ \{\mu\}_c \otimes \{\mu\}_s \right\}_{\{n\}_{cs}} \otimes \mathfrak{g}, \qquad n = n_1 + n_2$$

To be definite, consider fermionic identical nuclei (i.e., H).
Initial state (molecules at a very large distance):

$$|\Psi_i\rangle = \left| \left\{ \{\lambda_{i1}\}_c \otimes \{\tilde{\lambda}_{i1}\}_s \right\}_{\{1^{n_1}\}_{cs}};\ P_{i1} \right\rangle_1 \left| \left\{ \{\lambda_{i2}\}_c \otimes \{\tilde{\lambda}_{i2}\}_s \right\}_{\{1^{n_2}\}_{cs}};\ P_{i2} \right\rangle_2$$

$\{1^n_j\}$ denotes the antisymmetric IR of $\mathcal{S}_{n_j}$

Like in the case of the MS group, there are non-realizable permutations (of identical atoms between the molecules #1 and #2). We can expand the initial states in n-atomic, two-molecule states characterized by the induced representations of the group $\mathcal{S}_{n=n_1+n_2} \otimes \mathcal{I}$:

$$|\Psi_i\rangle = \sum_{\{\lambda\}} \alpha_\lambda \left| \left\{ \{\lambda\}_c \otimes \{\tilde{\lambda}\}_s \right\}_{\{1^n\}_{cs}};\ P_{12} \right\rangle_{12}, \qquad P_{12} = P_{i1} P_{i2}$$

At distances → ∞, all these states are degenerate. At closer distances (during the collision), this degeneracy is lifted. Therefore, after the collision (at $t \to \infty$ and again at distances → ∞) the expansion coefficients acquire different phases $\varphi_{\{\lambda\}}$:

$$|\Psi_i\rangle = \sum_{\{\lambda\}} \alpha_\lambda e^{i\varphi_{\{\lambda\}}} \left| \left\{ \{\lambda\}_c \otimes \{\tilde{\lambda}\}_s \right\}_{\{1^n\}_{cs}};\ P_{12} \right\rangle_{12}$$

Finally,

$$|\Psi_i\rangle = \sum_{\{\lambda_{f1,2}\}} \sum_{P_{f1,2}} \beta^{P_{f_1}\,P_{f_2}}_{\{\lambda_{f1}\}\,\{\lambda_{f2}\}} \left|\left\{\{\lambda_{f1}\}_c \otimes \{\tilde{\lambda}_{f1}\}_s\right\}_{\{1^{n_1}\}_{cs}};\ P_{f1}\right\rangle_1 \times$$

$$\left|\left\{\{\lambda_{f2}\}_c \otimes \{\tilde{\lambda}_{f2}\}_s\right\}_{\{1^{n_2}\}_{cs}};\ P_{f2}\right\rangle_2 ,$$

$$P_{f_1}P_{f_2} = P_{i1}P_{i2}$$

Coefficients $\beta^{P_{f_1}\,P_{f_2}}_{\{\lambda_{f1}\}\,\{\lambda_{f2}\}}$ with $\{\lambda_{f1,2}\} \neq \{\lambda_{i1,2}\}$ and $P_{f1,2} \neq P_{i1,2}$ are usually small. Therefore, inelastic collisions are usually slow.
For example, equilibration of para-H_2 to the $3:1$ ortho/para mixture at normal conditions (room temperature, 1 atm pressure) takes days without a catalyst.