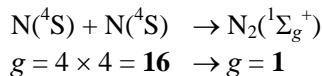


2. Electronic States of Atoms and Molecules

Why?

- electronic degeneracy contributes the equilibrium constant by **1/16** for the reaction;



2.1 Atoms

⟨Energy levels⟩

[One-electron system (hydrogenic atoms)]

(exact except for relativistic effect)

$$E_n = -\frac{hc_0 \mathcal{R}}{n^2} \quad (2.1)$$

$$n: \text{principal q. n.}, \quad \mathcal{R} = Z^2 \frac{\mu}{m_e} R_\infty, \quad R_\infty = \frac{m_e e^4}{8\varepsilon_0^2 h^3 c_0} = 109737.31568525(73) \text{ cm}^{-1} \text{ (Rydberg const.)}$$

[Multi-electron system]

- Cumulative database: <http://physics.nist.gov/PhysRefData/ASD/index.html>

Problem-2.1

Calculate the wavenumbers [cm^{-1}] of Lyman- α ($n = 2 \leftrightarrow 1$) transition of hydrogen (^1H) atom. ($m_e = 9.1094 \times 10^{-31} \text{ kg}$ and $m_p = 1.67262 \times 10^{-27} \text{ kg}$)

⟨Spectral term and degeneracy⟩

- Spectral term;

$$^{2S+1}[L]_J^{(o)}$$

S : electron spin q. n.

L : electron orbital angular momentum q. n.

[L]: symbolic representation of L (S, P, D, F, G, H, \dots for $L = 0, 1, 2, 3, 4, 5, \dots$)

J : total angular momentum q. n. ($J = |L - S|, |L - S| + 1, \dots, L + S$)

- Total degeneracy = spin degeneracy \times angular momentum degeneracy

$$g_{LS} = (2S + 1)(2L + 1) \quad (2.2)$$

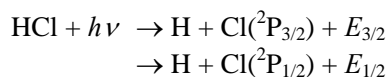
- Degeneracy of fine-structure state;

$$g_J = 2J + 1 \quad (2.3)$$

[Exercise-2.1] Fill the blanks in the table.

term	L	S	g_{LS}	g_J	J	fine structure
^1D	2	0	5	5	2	($^1\text{D}_2$)
^2S	0	1/2	2	2	1/2	($^2\text{S}_{1/2}$)
^2P	1	1/2	6	[2 4	[1/2 3/2	$^2\text{P}_{1/2}$ $^2\text{P}_{3/2}$
^3P	1	1	9	[1 3 5	[0 1 2	$^3\text{P}_0$ $^3\text{P}_1$ $^3\text{P}_2$

[example]



statistical branching ratio

$$\begin{aligned} &2 \cdot \underline{4} \rho_{\text{trans}}(E_{3/2}) \\ &2 \cdot \underline{2} \rho_{\text{trans}}(E_{1/2}) \end{aligned}$$

2.2 Linear molecules

⟨State designation and degeneracy⟩

- Designation of electronic states;

$${}^{2S+1}[A]_{A+\Sigma}^{(\pm)}$$

A : projection of L to the molecular axis

Σ : projection of S to the molecular axis

$[A]$: symbolic representation of A ($\Sigma, \Pi, \Delta, \Phi, \dots$ for $A = 0, 1, 2, 3, \dots$)

- Total degeneracy;

$$g_{AS} = (2S + 1)g_A \quad (2.4)$$

$$g_A = 2 \text{ (for } A \neq 0) \text{ or } g_A = 1 \text{ (for } A = 0)$$

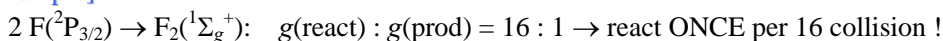
- Degeneracy of fine-structure state is NOT $2(A+\Sigma) + 1$

[e.g.] both ${}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$ states of NO are double degenerated

[Exercise-2.2] Fill the blanks.

desig.	A	Σ	g_{AS}	g_A	$A+\Sigma$	fine structure
${}^1\Delta$	2	0	2	2	2	
${}^2\Sigma$	0	1/2	2	1	$\pm 1/2$	
${}^2\Pi$	1	1/2	4	$\left[\begin{array}{l} 2 \\ 2 \end{array} \right.$	$\left[\begin{array}{l} 1/2 \\ 3/2 \end{array} \right.$	$\begin{array}{l} {}^2\Pi_{1/2} \\ {}^2\Pi_{3/2} \end{array}$
${}^3\Pi$	1	1	6	$\left[\begin{array}{l} 2 \\ 2 \\ 2 \end{array} \right.$	$\left[\begin{array}{l} 0 \\ 1 \\ 2 \end{array} \right.$	$\begin{array}{l} {}^3\Pi_0 \\ {}^3\Pi_1 \\ {}^3\Pi_2 \end{array}$

[example]



2.3 Non-linear molecules

⟨State designation and degeneracy⟩

- Designation of electronic states;

$${}^{2S+1}\Gamma$$

Γ : symmetry species of the electronic state ($A, A', A_2, B_1, E, F, \text{etc.}$)

- Total degeneracy;

$$g_{\Gamma S} = (2S + 1)g_{\Gamma} \quad (2.5)$$

$$g_{\Gamma} = 1, 2, 3, 4, 5, \dots \text{ for } \Gamma = [A, B], E, T(F), G, H, \dots$$

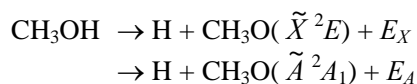
non-degenerates (A, B) and E of spherical group: \rightarrow no angular momentum

E of cylindrical group, $T[F], G, H, \dots$ of spherical group: \rightarrow (non-integer) angular momentum

[Exercise-2.2] Fill the blanks.

desig.	S	$g_{\Gamma S}$	g_{Γ}	fine structure
1T	0	3	3	
${}^2A'$	1/2	2	1	
2E	1/2	4	$\left[\begin{array}{l} 2 \\ 2 \end{array} \right.$	$\begin{array}{l} {}^2E_{1/2} \\ {}^2E_{3/2} \end{array}$

[example]



statistical branching ratio

$$2 \cdot \underline{4} \rho(E_X)$$

$$2 \cdot \underline{2} \rho(E_A)$$

Problem-2.2

Write degeneracy of following electronic states:

atom	ground state(s)	excited state(s)	molecule	ground state(s)	excited state(s)
F	$^2P_{3/2}, ^2P_{1/2}$	$^4P_{5/2}, ^4P_{3/2}, ^4P_{1/2}$	OH	$^2\Pi_{3/2}, ^2\Pi_{1/2}$	$^2\Sigma^+$
C	$^3P_0, ^3P_1, ^3P_2$	1D	CO	$^1\Sigma^+$	$^1\Pi$
Ca	1S	$^3P_0, ^3P_1, ^3P_2$	O ₂	$^3\Sigma_g^-$	$^1\Delta_g$
Al	$^2P_{1/2}, ^2P_{3/2}$	2S	CH	$^2\Pi_{1/2}, ^2\Pi_{3/2}$	$^2\Delta_{3/2}, ^2\Delta_{5/2}$
N	4S	$^2D_{5/2}, ^2D_{3/2}$	IBr	$^1\Sigma^+$	$^3\Pi_1, ^3\Pi_0^+$