2. Electronic States of Atoms and Molecules

Why?

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

$N(^4S) + N(^4S) \rightarrow N_2(^1\Sigma_g^+)$

$g = 4 \times 4 = \mathbf{16} \rightarrow g = \mathbf{1}$

2.1 Atoms

⟨Energy levels⟩

[One-electron system (hydrogenic atoms)]

(exact except for relativistic effect)

$$E_n = -\frac{hc_0\Re}{n^2} \qquad (2.1)$$

n: principal q. n., $\Re = Z^2 \frac{\mu}{m_e} R_\infty$, $R_\infty = \frac{m_e e^4}{8\varepsilon_0^2 h^3 c_0}$ = 109737.31568525(73) cm^{-1} (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 = 9.1094×10^{-31} kg and $m_p = 1.67262 \times 10^{-27}$ 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, ... for L = 0, 1, 2, 3, 4, 5, ...)

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

· Total degeneracy = spin degeneracy × angular momentum degeneracy

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

· Degeneracy of fine-structure state;

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

[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	($^1D_2$)
^2S	0	1/2	2	2	1/2	($^2S_{1/2}$)
^2P	1	1/2	6	2	1/2	$^2P_{1/2}$
				4	3/2	$^2P_{3/2}$
^3P	1	1	9	1	0	$^3P_0$
				3	1	$^3P_1$
				5	2	$^3P_2$

[example] statistical branching ratio

$HCl + h\nu \rightarrow H + Cl(^2P_{3/2}) + E_{3/2}$ $2 \cdot \underline{\mathbf{4}}\ \rho_{trans}(E_{3/2})$

$\rightarrow H + Cl(^2P_{1/2}) + E_{1/2}$ $2 \cdot \underline{\mathbf{2}}\ \rho_{trans}(E_{1/2})$

2.2 Linear molecules

⟨State designation and degeneracy⟩

· Designation of electronic states;

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

Λ: projection of L to the molecular axis
Σ: projection of S to the molecular axis
$[\Lambda]$: symbolic representation of Λ (Σ, Π, Δ, Φ, ... for Λ = 0, 1, 2, 3, ...)

· Total degeneracy;

$$g_{\Lambda S} = (2S + 1)g_\Lambda \qquad (2.4)$$

$g_\Lambda = 2$ (for $\Lambda \neq 0$) or $g_\Lambda = 1$ (for $\Lambda = 0$)

· Degeneracy of fine-structure state is NOT $2(\Lambda+\Sigma) + 1$
[*e.g.*] both $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states of NO are double degenerated

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[Exercise-2.2] Fill the blanks.

desig.	Λ	Σ	$g_{\Lambda S}$	g_Λ	$\Lambda+\Sigma$	fine structure
$^1\Delta$	2	0	2	2	2	
$^2\Sigma$	0	1/2	2	1	±1/2	
$^2\Pi$	1	1/2	4	2	1/2	$^2\Pi_{1/2}$
				2	3/2	$^2\Pi_{3/2}$
$^3\Pi$	1	1	6	2	0	$^3\Pi_0$
				2	1	$^3\Pi_1$
				2	2	$^3\Pi_2$

[example]
2 F($^2P_{3/2}$) → $F_2(^1\Sigma_g^+)$: g(react) : g(prod) = 16 : 1 → react ONCE per 16 collision !

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, *etc.*)

· Total degeneracy;

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

g_Γ = 1, 2, 3, 4, 5, ... for Γ = [A, B], E, $T(F)$, G, H, ...
non-degenerates (A, B) and E of spherical group: → no angular momentum
E of cylindrical group, $T[F]$, G, H, ... of spherical group: → (non-integer) angular momentum

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[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	2	$^2E_{1/2}$
			2	$^2E_{3/2}$

[example] statistical branching ratio

$CH_3OH \rightarrow H + CH_3O(\tilde{X}\,^2E) + E_X$ $\quad 2\cdot\underline{\mathbf{4}}\,\rho(E_X)$
$\rightarrow H + CH_3O(\tilde{A}\,^2A_1) + E_A$ $\quad 2\cdot\underline{\mathbf{2}}\,\rho(E_A)$

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	$^1\Sigma^+$	$^3\Pi_1$, $^3\Pi_0^+$