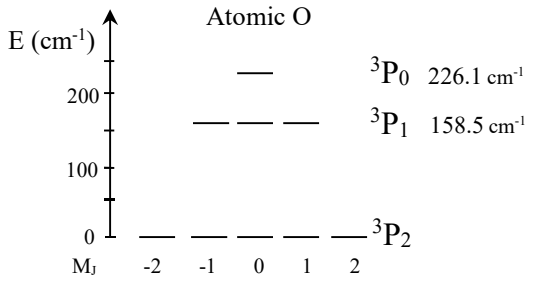
Electronic Degree of Freedom

$$q_e = \sum_{\text{all energy levels}} g_i\, e^{-E_i/kT}$$

with $E_{gs} = 0$ as the reference energy



Ground State Atomic Terms, Low Lying Excited States, and Degeneracies (g_i).

Element	H	B	C	N	O	F	P	S	Cl	Br
Term	$^2S_{½}$	$^2P_{½}$	$^3P_0$	$^4S_{3/2}$	$^3P_2$	$^2P_{3/2}$	$^4S_{3/2}$	$^3P_2$	$^2P_{3/2}$	$^2P_{3/2}$
g_{gs}	2	2	1	4	5	4	4	5	4	4
Excited states										
E (cm^{-1})		15.254	16.4		158.5	404		396.8	881	
g_{ex}		4	3		3	2		3	2	
E(cm^{-1})			43.5		226.1			573.6		
g_{ex}			5		1			1		
q_e at 298.15 K	2	5.71615	7.82505	4	6.73212	4.28470	4	5.50495	4.02850	4

Example: ground state O: $2p^4$: ↑↓ (2s) ↑↓ ↑ ↑ (2p)

$^3P_2$ $J = 2$ $M_J = -2,-1,0, 1, 2$ $g_{gs} = 5$

$q_e = 5 + 3\, e^{-158.5/207.2} + 1\, e^{-226.1/207.2} = 5 + 1.39404 + 0.33581 = 6.72984$

For almost all molecules the energy of the first excited state is >> kT above the ground state, only the ground state contributes and the partition function is well approximated by the ground state degeneracy at 298.2 K, $q_e \cong g_{gs}$

O_2: $1\sigma_g^2\, 1\sigma_u^{*2}\, 2\sigma_g^2\, 2\sigma_u^{*2}\, 3\sigma_g^2\, 1\pi_u^4\, 1\pi_g^{*2}$ $^3\Sigma_g^-$, $g_{gs} = 3$ $q_e = 3$

$^1\Delta_g$, $g_{ex} = 2$ at 7918.1 cm^{-1} and $^1\Sigma_g^+$, $g_{ex} = 1$ at 13195.1 cm^{-1}

Molecular Exception: NO: $1\sigma^2\, 1\sigma^{*2}\, 2\sigma^2\, 3\sigma^{*2}\, 2\sigma^2\, 1\pi^4\, 1\pi^{*1}$

$^2\Pi_{½}$, $g_{gs} = 2$ and $^2\Pi_{3/2}$, $g_{ex} = 2$ at 119.8 cm^{-1} $q_e = 2 + 2\, e^{-119.8/207.2} = 3.156$

Total Molecular Angular Momentum: $\Omega = \Lambda + \Sigma$, $|\Lambda - \Sigma|$

for NO, $\Lambda = 1$ with $M_\Lambda = +1, -1$ and $\Sigma = ½$ with $M_\Sigma = +½, -½$ → two terms $^2\Pi_{3/2}$ and $^2\Pi_{½}$

M_Λ	M_Σ	M_Ω	
1	½	3/2	$^2\Pi_{3/2}$
1	-½	½	$^2\Pi_{½}$
-1	½	-½	
-1	-½	-3/2