Equations - Quantum Chem 4

Energy

Quick and dirty conversions

$E_{kcal/mol} = 2.86x10^4/\lambda_{(nm)} = 9.52x10^{-14} \times \upsilon_{(hz)}$
$E_{eV} = 1240/\lambda_{(nm)}$
$\tilde{v} = 349.8\ x\ E_{(kcal/mol)}$

Hydrogen

$$\hat{H} = \frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{e^2}{4\pi\varepsilon_0 r_{A1}} - \frac{e^2}{4\pi\varepsilon_0 r_{B1}} + \frac{e^2}{4\pi\varepsilon_0 r_{AB}}$$

$E_\sigma = E_{H_{1s}} + \frac{j_0}{R} - \frac{j+k}{1+s}$; $E_{\sigma^*} = E_{H_{1s}} + \frac{j_0}{R} - \frac{j-k}{1-s}$;

$j = j_o \int \frac{\psi_A^2}{r_B}\, d\tau$ (coulomb integral); $k = j_o \int \frac{\psi_A \psi_B}{r_B}\, d\tau$ (exchange integral); $s = j_o \int \frac{\psi_A \psi_B}{r_B}\, d\tau$ *(overlap integral)*

½ (N-N*) = bond order

$\mu_i = er$ (e-charge, r-separation) Transition dipole moment - classical
$\mu_{fi} = <\psi_1|u_i|\psi_2>^2$ Transition dipole moment – QM
$\mu_{fi} = \int \psi_f^* \hat{\mu} \psi_i\, d\tau$ (ψ_f – final wf, $\hat{\mu}$ – dipole operator, ψ_i – initial wf)
tdm is 0 if transition is forbidden. If non-zero, then transition is allowed
$\Gamma_{1\to 2} \propto \rho[<\psi_1|u_i|\psi_2>]^2$

Angular Momentum

$L = l(l+1)^{\frac{1}{2}}\hbar$; $L_z = m_s \hbar$ where $l \in \mathbb{N}$

Spin Angular Momentum

$S = (s(s+1))^{½}\hbar$; $S_z = m_s \hbar$ where $s \in \{\frac{1}{2}, -\frac{1}{2}\}$

For 1 electron - $S = \frac{\sqrt{3}}{2}\hbar$; $m_z = \pm\frac{1}{2}\hbar$
For 2 electrons – $S = 0, S_z = 0$ singlet
$S = \sqrt{2\hbar}, S_z = -\hbar, 0, \hbar$ triplet

A = ϵcl (ϵ-extinction coeff, c-conc, l-path length, absorption) Beer-Lambert law

$A = -\log_{10}(T) = -\log_{10}(\frac{I_O}{I_I})$

$f = 4.3x10^{-9} \int \epsilon(\tilde{v}) d\,\tilde{v} \approx 4.3x10^{-9}\, \epsilon_{max} \Delta\tilde{v}_{\frac{1}{2}}$ - Oscillator strength

Spin-orbit coupling

$H_{SO} = \zeta_{SO}\mu_S\mu_L$; ζ_{SO} spin – orbit coupling constant, μ_S spin mag moment, μ_L orbit mag moment

$\zeta_{SO} \propto \sum_K \frac{Z_K}{r_{iK}^3}$ Z_K charge on each at nucleus, r_{iK} distance between e^- and nucleus

So, ζ_{SO} approximately scales with ~ Z_K^4. It scales very strongly with atomic size!

Stat Mech

$W = {N!}/{N_i!\,N_j!\,\ldots N_p!}$

$$\ln(W) = N ln N - \sum_i N_i ln N_i; \qquad \ln(N!) \approx N ln N - N$$

Relative populations of two degenerative states

$\frac{N_i}{N_f} = \frac{g_i}{g_f} e^{\frac{-(\epsilon_f - \epsilon_i)}{kT}} = \frac{g_i}{g_f} e^{\frac{-(\tilde{v}_f - \tilde{v}_i)}{k_{\tilde{v}} T}}$ $\quad k_{\tilde{v}} = 0.694468; k = 1.38x10^{-23}$