WLAM: Calculation of the Coupled Potential

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I. COUPLED VIBRATIONAL POTENTIALS

Both coulped vibrational potentials and multi-moments, including spherical and non-spherical polarizabilited and qudrupole, etc., can be expressed as

$$I = \int_0^\infty \psi_v^*(R) f(R) \psi_{v'}(R)\, dR \tag{1}$$

where $f(R)$ denotes the potentials or multi-moments, which is varied as the internuclear distance R. ψ are the molecular vibrational wavefunctions. Since $R > 0$, both ψ and $f(R)$ do not exist as $R < 0$, and we can take them as zero. So, Eq. (**??**) can be written as

$$I = \int_{-\infty}^\infty \psi_v^*(R) f(R) \psi_{v'}(R)\, dR \tag{2}$$

Eq. (**??**) can be solved by using Gauss-Hermite quadratures. However, Gauss-Hermite quadratures are for the whole $(-\infty \sim \infty)$ range, while we can get limited $f(R)$. In order to use Gauss-Hermite quadratures, we have to suppose that $f(R)$ is smooth within the whole range.

Suppose we have N Gauss-Hermite quadratures: ξ_1, ξ_2, $\ldots$, ξ_N,Eq. (**??**) should be

$$I = \sum_{k=1}^{N} \lambda_k g(\xi_k) \exp\left({\xi_k}^2\right) \tag{3}$$

where λ_k is the weighted factor[**?**]. $g(R)$ is the integrand.

$$g(R) = \psi_v^*(R) f(R) \psi_{v'}(R) \tag{4}$$

If $g(R)$ are got only within $[R_1, R_M]$, we have to map Gauss-Hermite quadratures into this range. Suppose

$$R = R_\alpha \times \left(\frac{X}{\alpha} + R_x\right) \times R_e \tag{5}$$

where α and R_e are constants, while R_α and R_x are transforming coefficients to ensure R on every quadrature X is within $[R_1, R_M]$. So

$$\begin{aligned} I &= \int_{-\infty}^\infty g\left[R_\alpha \times \left(\frac{X}{\alpha} + R_x\right) \times R_e\right] d\left[R_\alpha \times \left(\frac{X}{\alpha} + R_x\right) \times R_e\right] \\ &= \frac{R_\alpha \times R_e}{\alpha} \int_{-\infty}^\infty g\left[R_\alpha \times \left(\frac{X}{\alpha} + R_x\right) \times R_e\right] dX \end{aligned} \tag{6}$$

Notice that the integral varialbe of R is turned to X. By using Eq.(**??**), we get,

$$I = \frac{R_\alpha \times R_e}{\alpha} \sum_{k=1}^{N} \lambda_k g\left[R_\alpha \times \left(\frac{\xi_k}{\alpha} + R_x\right) \times R_e\right] \exp\left({\xi_k}^2\right) \tag{7}$$

For simplicity, we let,

$$f_a = \frac{R_\alpha \times R_e}{\alpha} \tag{8}$$

$$\zeta_k = R_\alpha \times \left(\frac{\xi_k}{\alpha} + R_x\right) \times R_e \tag{9}$$

the integral is then written as,

$$\begin{aligned} I &= f_a \times \sum_{k=1}^{N} \lambda_k g(\zeta_k) \exp\left({\xi_k}^2\right) \\ &= f_a \times \sum_{k=1}^{N} \lambda_k \psi_\upsilon(\zeta_k) f(\zeta_k) \psi_{\upsilon'}(\zeta_k) \\ &\times \exp\left[\left(\alpha \times \frac{\zeta_k - R_\alpha \times R_e \times R_x}{R_\alpha \times R_e}\right)^2\right] \end{aligned} \tag{10}$$

So, if we choose suitalbe transforming coefficients R_α and R_x to ensure every ζ_k in Eq.(**??**) is within $[R_1, R_M]$, we can interpolate every $\psi_\upsilon(\zeta_k)$, $\psi_{\upsilon'}(\zeta_k)$ and $f(\zeta_k)$.

If we choose another transforming formula, i.e.,

$$\alpha = R_\alpha \times \sqrt{\omega_e \times m_u} \times R_e \tag{11}$$

$$R = \left(\frac{X}{\alpha} + R_x\right) \times R_e \tag{12}$$

where R_α, ω_e, m_u, R_e and R_x are all constants. The integral is turned

$$\begin{aligned} I &= \int_{-\infty}^{\infty} g\left[\left(\frac{X}{\alpha} + R_x\right) \times R_e\right] d\left[\left(\frac{X}{\alpha} + R_x\right) \times R_e\right] \\ &= \frac{R_e}{\alpha} \int_{-\infty}^{\infty} g\left[\left(\frac{X}{\alpha} + R_x\right) \times R_e\right] dX \end{aligned} \tag{13}$$

letting

$$f_a = \frac{R_e}{\alpha} \tag{14}$$

$$\zeta_k = \left(\frac{\xi_k}{\alpha} + R_x\right) \times R_e \tag{15}$$

then the integral is

$$\begin{aligned} I &= f_a \times \sum_{k=1}^{N} \lambda_k g(\zeta_k) \exp\left({\xi_k}^2\right) \\ &= f_a \times \sum_{k=1}^{N} \lambda_k \psi_\upsilon(\zeta_k) f(\zeta_k) \psi_{\upsilon'}(\zeta_k) \\ &\times \exp\left[\left(\frac{\zeta_k}{R_e} - R_x\right) \times \alpha\right]^2 \end{aligned} \tag{16}$$

[] Both ξ_k and λ_k can be got through mathematical manual. Notice that λ_k are different for different N and ξ_k.