Classical approximation of nuclear motion - preliminary observations

Time-dependent version of SE for nuclei in BO approximation:

$$i\hbar\frac{\partial}{\partial t}\Phi(\mathbf{R},t) = [\mathbf{T}_n(\mathbf{R}) + E_{\mathbf{R}}]\Phi(\mathbf{R}) \qquad (1)$$

$\rightarrow$ can be solved for only a small number of nuclei (5-10)

$\rightarrow$ in many situations sufficient to treat nuclei classically.

Accuracy of classical approximation improves with

- increasing temperature
- increasing mass of nuclei

Worst case: Hydrogen bonded system at very low temperatures.

Classical approximation of nuclear motion - outline of derivation

Classical, i.e. Newtonian dynamics, can be formally derived from Eq. 1.

1. Write Φ in polar representation:

$$\Phi(\mathbf{R},t) = A(\mathbf{R},t)\exp(iS(\mathbf{R},t)/\hbar) \tag{2}$$

$A \in R > 0, S \in R$.

2. Insertion of Eq. 2 in Eq. 1 and separation of real and imaginary parts:

$$\frac{\partial S}{\partial t} + \sum_I \frac{1}{2M_I}\left(\nabla_I S\right)^2 + E_{\mathbf{R}} - \sum_I \frac{\hbar^2}{2M_I}\frac{\nabla_I^2 A}{A} = 0 \tag{3}$$

$$\frac{\partial A}{\partial t} + \sum_I \frac{1}{M_I}\left(\nabla_I S\right)\left(\nabla_I A\right) + \sum_I \frac{1}{2M_I} A \nabla_I^2 S = 0 \tag{4}$$

3. Take the limit $\hbar \to 0$ in Eq. 3:

$$\frac{\partial S}{\partial t} + \sum_I \frac{(\nabla_I S)^2}{2M_I} + E_{\mathbf{R}} = 0 \tag{5}$$

Notice, Eq. 5 is isomorph with the Hamilton-Jacobi Equation of classical mechanics.

4. Correspondence with classical mechanics

Identify phase $S(\mathbf{R}, t)$ with classical action $S^{cl}(\mathbf{R}, t)$.

Identify nuclear gradient of phase, $\nabla_I S$, with classical momentum, $\mathbf{p}_I$.

Eq. 5 becomes the Hamilton-Jacobi Equation of classical mechanics:

$$\frac{\partial S^{\mathrm{cl}}}{\partial t} + \sum_I \frac{\mathbf{p}_I^2}{2M_I} + E_{\mathbf{R}} = 0 \tag{6}$$

5. Hamilton and Newton equations of motion from Hamilton-Jacobi Equation

$$H = \sum_I \mathbf{p}_I^2/(2M_I) + E_{\mathbf{R}} \tag{7}$$

$$\dot{\mathbf{R}}_I = \partial H/\partial \mathbf{p}_I \tag{8}$$

$$\dot{\mathbf{p}}_I = -\partial H/\partial \mathbf{R}_I \tag{9}$$

Eq. 9 is Newton's second law of motion,

$$\mathbf{f}_I = M_I \ddot{\mathbf{R}}_I = -\nabla_I E_{\mathbf{R}}. \tag{10}$$