One-dimensional case

$$H = \frac{1}{2m} p^2 + \frac{1}{2} k q^2$$

$$\omega = \sqrt{\frac{k}{m}}$$

$$m \frac{d^2 q}{dt^2} = - \frac{\partial U}{\partial q}$$

$$\ddot{q} + \omega^2 q = 0$$

$$q = A \sin(\omega t) + B \cos(\omega t)$$

$$p = m \dot{q} = m\omega \left[A \cos(\omega t) - B \sin(\omega t) \right]$$

$$q_0 = q(t_0)$$

$$p_0 = p(t_0)$$

$$A = q_0 \sin(\omega t_0) + \frac{p_0}{m\omega} \cos(\omega t_0)$$

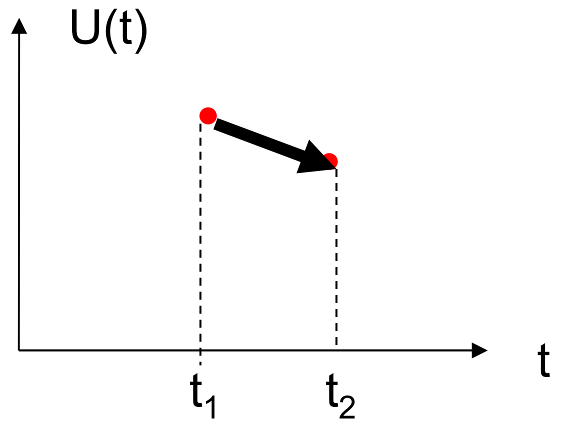
$$B = q_0 \cos(\omega t_0) - \frac{p_0}{m\omega} \sin(\omega t_0)$$

Finally

$$q = q_0 \cos(\omega (t - t_0)) + \frac{p_0}{m\omega} \sin(\omega (t - t_0))$$

$$p = m\omega \left[- q_0 \sin(\omega (t - t_0)) + \frac{p_0}{m\omega} \cos(\omega (t - t_0)) \right]$$

Coding



$$U(q) = \frac{1}{2}kq^2$$

$$\omega = \sqrt{\frac{k}{m}}$$

$$q(t_2) = q(t_1)\cos(\omega(t - t_1)) + \frac{p(t_1)}{m\omega}\sin(\omega(t - t_1))$$

$$p(t_2) = m\omega\left[-q(t_1)\sin(\omega(t - t_1)) + \frac{p(t_1)}{m\omega}\cos(\omega(t - t_1))\right]$$

Propagation from t2→t3

$$t_1 \to t_2$$
$$t_2 \to t_3$$

Initial condition

$$q_1 = q(t_1)$$
$$p_1 = p(t_1)$$

Multi-dimensional case

$$H = \sum_{i=1}^{N} \left[\frac{1}{2m_i} p_i^2 + \frac{1}{2} k_i q_i^2 \right]$$

$$\omega_i = \sqrt{\frac{k_i}{m_i}}$$

$$q_i(t_2) = q_i(t_1)\cos(\omega_i(t - t_1)) + \frac{p_i(t_1)}{m_i \omega_i}\sin(\omega_i(t - t_1))$$

$$p_i(t_2) = m_i \omega_i \left[-q_i(t_1)\sin(\omega_i(t - t_1)) + \frac{p_i(t_1)}{m_i \omega_i}\cos(\omega_i(t - t_1)) \right]$$

Propagation from t2→t3

$$t_1 \to t_2$$
$$t_2 \to t_3$$

Initial condition

$$q_{i1} = q_i(t_1)$$
$$p_{i1} = p_i(t_1)$$

Say chose N=3

$$\omega_1 = 100\ cm^{-1}$$

Typical for motion of dihedral angle vibration

$$\omega_2 = 1500\ cm^{-1}$$

Typical for motion of bending vibration

$$\omega_3 = 3500\ cm^{-1}$$

Typical for motion of C-H stretching vibration

In general when omiga is bigger, time step size has to be smaller. When dynamics is governed by C-H stretching, you may need delta-t =0.1 fs (or smaller)

(1) Compare your on-the-fly code with this exact solution to see if your code is OK

(2) If your code is OK, please check when accumulative error is big after 100fs, 1000fs, or 2000fs with given time step-size.

(3) Balance time step-size with your dynamics, say if your dynamics takes 100fs to be finished, you can have delta-t=0.5fs, if 1000fs, you may need 0.1fs