PH: 322 Molecular Simulation Homework 1 **Due 27th Jan, 2016**

1. Recall that both electron and nuclei move quantum mechanically in time dependent effective potentials which are obtained self consistently. The product ansatz gives the following equation for nuclei

$$i\hbar\frac{\partial}{\partial t}\chi=-\sum_I\frac{\hbar^2}{2M_I}\nabla_I^2\chi+\left\{\int dr\Psi^*H_e\Psi\right\}\chi$$

For classical dynamics of nuclei assume $\chi=A(R_I,t)\,e^{\frac{i}{\hbar}S(R_I,t)}$

Show that

$$\frac{\partial S}{\partial t}+\sum_I\frac{1}{2M_I}(\nabla_I S)^2+\int dr\Psi^*H_e\Psi=\hbar^2\sum_I\frac{1}{2M_I}\frac{\nabla_I^2A}{A}$$

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

2. Show that volume in phase space is preserved under Hamiltonian dynamics.

3. Show that Liouville operator (L) is hermitian : $L=L^\dagger$

4. Define the propagator $U(t) = exp(iLt)$

(a) Show that it is a unitary operator

$$U^\dagger(t)U(t) = I$$

(b) Show that determinant of U(t) is 1

(c) Define propagator $U(\delta t)$ for small time step δt . Show $U^\dagger(\delta t)= U(-\delta t) = U^{-1}(\delta t)$ and $U(-\delta t)\, U(\delta t) = I$

5. Write the Liouville operator as follows

$$iL=\frac{p}{m}\frac{\partial}{\partial x}+F(x)\frac{\partial}{\partial p}=iL_1+iL_2$$

$$iL_1=\frac{p}{m}\frac{\partial}{\partial x}\qquad iL_2=F(x)\frac{\partial}{\partial p}$$

Show that iL_1 and iL_2 do not commute: $[iL_1,iL_2]\neq 0$.

6. Consider the case of simple harmonic oscillator

$$F(x)=-\omega^2x$$

Using the position Verlet or leap-frog scheme do the linear stability analysis of the equation of motion. The stability analysis will give you limit on the time step δt to be used in the simulation (you may consult Siam. J. comp. 18, 203 (1997)).

6. Derive the classical propagator for a multiple time step (MTS) integration scheme. Also derive Verlet like equation for the MTS integration scheme. (JCP, **97,** 1990 (1992))

7. Derive the equation of motion for a fourth order predictor-corrector scheme using Trotter formalism as was done for Verlet scheme in the class. You may consult JCP, 102, 8071, (1995)