CHM1465: Foundations of Molecular Simulation

PROBLEM SET 4

Notes:

- This set contains 3 problems.
- This fourth and final set is due in two weeks, December 3, 2008.

1. For a harmonic oscillator system with Hamiltonian $H = \frac{1}{2}(p^2 + q^2)$, compare the critical points of instability Δt_c of the Verlet, HOA2, FR4, and 4th-order order Suziki (gradient corrected) integrators.

2. Consider an anharmonic oscillator system in three dimensions with Hamiltonian

$$H = \frac{\vec{p}_1 \cdot \vec{p}_1}{2m_1} + \frac{\vec{p}_2 \cdot \vec{p}_2}{2m_2} + U(r_{12}) \qquad U(r_{12}) = \frac{k}{2} r_{12}^2 + \frac{\lambda}{4} r_{12}^4,$$

where $r_{12} = |\vec{r}_2 - \vec{r}_1|$, k is large and λ is small.

   (a) Show that the Hamiltonian can be recast in centre-of-mass $\vec{R}$ and relative coordinates $\vec{r} = \vec{r}_{12}$ as

$$H = \frac{\vec{P} \cdot \vec{P}}{2M} + \frac{\vec{p} \cdot \vec{p}}{2\mu} + U(r) = K_P + K_p + U,$$

   where M is the total mass of the system, μ is the relative mass, and $\vec{P}$ and $\vec{p}$ are the momenta conjugate to $\vec{R}$ and $\vec{r}$, respectively.

      i. What are the solutions of the equations of motion for $\vec{R}$ and $\vec{P}$?

      ii. Construct the Liouville operators $\mathcal{L}_P$, $\mathcal{L}_p$ and $\mathcal{L}_U$ and evaluate the commutators of these three operators.

   (b) Devise a second-order symplectic integrator of this system and find the shadow Hamiltonian to order Δt^2.

   (c) Suppose one writes the potential $U = U_h + \Delta U$ in terms of a harmonic reference potential $U_h(r) = kr^2/2$ and a difference potential $\Delta U(r) = \lambda r^4/4$. Use a splitting scheme to construct a second-order integrator that uses the *exact solution* of the evolution of a harmonic oscillator. To order Δt^2, what does the shadow Hamiltonian look like for this integrator? Is it better, or worse, than the integrator in part b?

   (d) Suppose the actual potential energy $U_A(r)$ and forces are computed using a costly electronic structure method. Using the potential $U(r)$ as a reference potential, where $U_A(r) \approx U(r)$, devise an integrator using splitting methods that minimizes the number of electronic structure calculations over a fixed time interval. How might multiple time step methods be used profitably in this integrator?

3. An important dynamical property of molecules in a fluid is the *self-diffusion coefficient* D, that is a measure of how quickly each particle in the fluid moves through space. For a system of N particles, it can be calculated in two different ways:

   - One can integrate the velocity autocorrelation function:

     $$D = \frac{1}{3N} \sum_{i=1}^{N} \int dt' \, \langle \vec{v}_i(t) \cdot \vec{v}_i(t+t') \rangle \,,$$

     where $\vec{v}_i(t)$ is the velocity of particle i at time t. Note that in a simultation, both t and $t+t'$ are computed at intervals of the timestep Δt.

   - One can use the relation

     $$D = \lim_{t' \to \infty} \sum_{i=1}^{N} \frac{\langle |\vec{r}_i(t+t') - \vec{r}_i(t)| \rangle}{6Nt'},$$

     where $\vec{r}_i(t)$ is the position of particle i at time t. Note that when using this form, one must pay careful attention to how the distance grows in a periodic system.

   Modify the code you wrote for a Lennard-Jones system (or modify the sample code provided on the class web site) to compute the self-diffusion coefficient D in the two ways mentioned above. The system conditions can be taken to be as described in problem 3 on problem set 3.