Tutorial MWQC 2022

1. (a) You are asked to simulate liquid water using SPC model. The box dimensions are given as 2nm x 2nm x 2nm. How many water molecules do you have to fill the box with? (Calculate; do not guess!!)

   (b) In a simulation the **reference** temperature is 300 K. At a given instant the observed temperature is 290 K. What will be the velocity re-scaling factor? Assume that you are using instantaneous velocity re-scaling to adjust the temperature.

2. (a) Transform the time-dependent Schrödinger equation into its time-independent form.

   (b) Show that for a time independent Hamiltonian, solving the Schrödinger equation reduces to solving the eigenvalue equation for the Hamiltonian.

3. Suppose $\phi_n(r; R), n = 1, 2, ...$ are the adiabatic or Born-Oppenheimer electronic states of a molecule where r and R represent the electronic and nuclear coordinates respectively, i.e., $\hat{H}_e\phi_n(r; R) = E_n(R)\phi_n(r; R)$, where $\hat{H}_e$ is the electronic Hamiltonian parametrically dependent on R.

   (a) Show that

   $$\nabla_R E_n = \langle \phi_n(r; R)|\nabla_R \hat{H}_e|\phi_n(r; R)\rangle$$

   This is referred to as the Hellman-Feynmann theorem. It is used to calculate forces on the nuclei moving on a potential energy surface or to calculate analytic derivatives for geometry optimization in quantum chemistry programs.

   (b) Show that the non-adiabatic coupling vector

   $$\langle \phi_i(r; R)|\nabla_R \phi_j(r; R)\rangle = \frac{\langle \phi_i(r; R)|\nabla_R \hat{H}_e|\phi_j(r; R)\rangle}{E_j - E_i}$$

   This expression for the non-adiabatic coupling is useful in several nuclear dynamics methods including surface hopping.

   (c) Consider a system whose electronic state which is a linear combination of Born-Oppenheimer states, i.e., $\Psi(r; R) = \sum_i c_i\phi_i(r; R)$. The Ehrenfest method describes the motion of the nuclei of this system on

an effective potential given by $V = \langle \Psi | \hat{H}_e | \Psi \rangle$. Write an expression for the forces in this case in terms of adiabatic forces and derivative couplings.

4. Prove that $\exp[A + B] \neq \exp[A].\exp[B]$ when $[A, B] \neq 0$.

5. For two diabats $V_1 = 0.5m\omega^2(x - x_0)^2$ and $V_2 = 0.5m\omega^2(x + x_0)^2$ with a constant coupling V_c, calculate the adiabatic energies $E(x)$ and eigenfunctions $\phi_i(x)$. Thereby calculate the derivative coupling $d_{12}(x) = \langle \phi_1 | \frac{\partial}{\partial x} \phi_2 \rangle$.

6. Consider a potential $V(x, y)$ given by:

$$V = 0.5m\omega^2(x^2 + y^2) + \begin{pmatrix} gx & gy \\ gy & -gx \end{pmatrix} \quad (1)$$

   (a) Find the eigenvalues and eigenfunctions (ψ_i) as a function of x, y.

   (b) Transform the eigenfunctions to radial polar coordinates: $x = r\cos(\phi), y = r\sin(\phi)$ and calculate the derivative coupling. $d_{12}(r, \phi) = \langle \psi_1 | \frac{\partial}{\partial \phi} \psi_2 \rangle$

   (c) Show that integral of $d_{12}(r, \phi)$ over a closed contour gives π.

7. In classical mechanics one can formulate the dynamics in terms of phase space density - the so called Liouvillian approach. So, the question one wants to answer is that if we have an initial phase space density $\rho(x, p, t = 0)$ of interest then what is the time evolved density $\rho(x, p, t)$? Note that we will be using a one degree of freedom (hence two dimensional phase space) notation for this entire problem. A formal solution to the Liouville's equation can be written as follows:

$$\rho(x, p, t) = \int \int dx' dp' \delta[x - x_t(x', p')]\delta[p - p_t(x', p')]\rho(x', p', 0) \quad (2)$$

with (x_t, p_t) being the classical trajectory at time t, obtained by integrating the equations of motion with initial conditions (x', p'). For certain simple cases one can evaluate the above to obtain the evolved densities.

   (a) Suppose the initial density is uniform i.e., $\rho(x', p', 0) = 1/N$ with N being the total number of trajectories. In other words, every trajectory gets the same weight of $1/N$. Obtain a suitable expression for $\rho(x, p, t)$. Provide an interpretation for your result.

   (b) Let us now consider the case of a nonuniform initial density. So, we take the initial normalized phase space density as

$$\rho(x', p', 0) = \frac{1}{\pi\hbar} \exp(-(x' - x_0)^2/2\sigma_{x'}^2) \exp(-(p' - p_0)^2/2\sigma_{p'}^2) \quad (3)$$

   which corresponds to a minimum uncertainty wavepacket centered around (x_0, p_0). What this means is that, instead of the initial conditions being uniformly distributed, they are gaussian distributed

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around (x_0, p_0) with $\sigma_{x'}\sigma_{p'} = \hbar/2$. Such types of initial densities are very useful in comparing the results of classical and quantum dynamics for a given system. For simplicity, take the system to be a free particle of mass m and obtain an expression for the time evolved density. Does this result make intuitive sense to you?

(c) Using $\rho(x, p, t)$ we can now determine the reduced space densities. For example the momentum space density is obtained as

$$\tilde{\rho}(p, t) = \int dx \rho(x, p, t) \tag{4}$$

and a similar expression for the coordinate space density $\tilde{\rho}(x, t)$. Show that for the free particle case

$$\tilde{\rho}(p, t) = \frac{1}{\sigma_{p'}\sqrt{2\pi}} \exp(-(p - p_0)^2/2\sigma_{p'}^2) \tag{5}$$

With a bit more effort show that

$$\tilde{\rho}(x, t) = \frac{1}{\sigma_t \sqrt{2\pi}} \exp\left[-\left(x - x_0 - \frac{p_0 t}{m}\right)^2 / 2\sigma_t^2\right] \tag{6}$$

with a suitable definition for σ_t. Do the above reduced space densities make sense for a free particle? Can you think of a reason or two as to why is it important to compute the reduced space densities?

You need to perform certain gaussian integrals to obtain the above results. Thus,

$$\int_{-\infty}^{\infty} dz e^{-\lambda z^2} = \sqrt{\frac{\pi}{\lambda}} \tag{7}$$

8. Consider the unimolecular dissociation reaction of H_2CO to H_2 and CO. The barrier height V_0 is about 93.6 kcal mol^{-1}. The vibrational mode frequencies (in cm^{-1}) for the reactant are $2843, 2766, 1746, 1501, 1247$, and 1164. For the transition state (TS) the relevant frequencies are $2760, 1654, 1137, 941, 697$, and a single imaginary frequency $2288i$. Remember that a simple TS is expected to have one purely imaginary mode frequency.

(a) Taking the zero point energy at the TS into account calculate the threshold energy for the reaction.

(b) Estimate the RRK rate constant in ps^{-1} at an energy of $E = 110$ kcal mol^{-1}. Use the threshold energy value obtained above.

(c) At an energy of $E = 110$ kcal mol^{-1} count the number of bound state at the TS. Idenitfy these states by their respective quantum numbers.

(d) The classical RRKM rate expression can be written down as

$$k(E) = \frac{(s-1)! \prod_{j=1}^{s} \hbar \omega_j}{2\pi \hbar E^{s-1}} \sum_{\mathbf{n}} h \left[E - V_0 - \hbar \omega^{\ddagger} \cdot \left(\mathbf{n} + \frac{1}{2} \right) \right] \quad (8)$$

where the summation above is over the quantum numbers corresponding to the bound states at the TS. The function $h[z]$ is the Heaviside function, hence $h[z] = 1$ for $z > 0$ and zero otherwise. In the above expression, the frequencies ω_j correspond to the reactant whereas the $\omega^{\ddagger}$ correspond to those at the TS [except, of course, the imaginary one!]. Using the expression above estimate the RRKM rate at $E = 110$ kcal mol^{-1}. How does this compare to the RRK rate?

9. Consider the inverted simple harmonic oscillator Hamiltonian

$$H(q,p) = \frac{1}{2m}p^2 - \frac{1}{2}m\omega^2 q^2 \quad (9)$$

Express the Hamilton's equations of motion as

$$\dot{q} = \frac{\partial H}{\partial p} \equiv f(q,p)$$

$$\dot{p} = -\frac{\partial H}{\partial q} \equiv g(q,p) \quad (10)$$
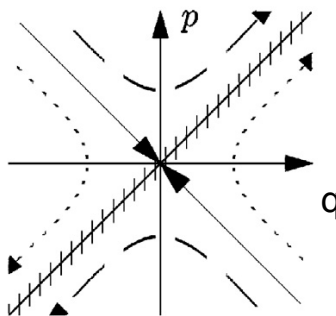

Figure 1: Phase space for the inverted harmonic oscillator i.e., a harmonic barrier. Note the separatrix, which divides reactant region from product region, and the sample trajectories. The notion of a transition state is dynamically associated with the separatrix - a phase space structure. One thinks of the transition state as a condition of dynamical instability.

(a) Find the points in phase space (q^*, p^*) such that $\dot{q} = 0 = \dot{p}$. In dynamical systems theory such points are known as the *fixed points* of the flow.

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(b) Now *linearize* the equations of motion about the fixed points. In other words expand $f(q, p)$ and $g(q, p)$ around (q^*, p^*) up to linear order in the deviations from the fixed point. Denoting the phase space variables as $\mathbf{z} \equiv (q, p)$, show that one can write the linearized flow as $\delta\dot{\mathbf{z}} = \mathbf{M}\delta\mathbf{z}$ with $\mathbf{M}$ being a 2×2 matrix and $\delta\mathbf{z} = \mathbf{z} - \mathbf{z}^*$. Check that the trace and determinant of the matrix $\mathbf{M}$ are zero and $-\omega^2$ respectively. Such fixed points are called as *saddles*.

(c) Defining energy scales such that the barrier top corresponds to $E \equiv E^{\ddagger} = 0$, find the equations for the curves in phase space for initial conditions having the total energy $E = 0$. These curves yield the so called *separatrix*.

(d) Solve the equations of motion exactly for a given initial condition (q_0, p_0) at $t = 0$. Using the exact solution for $q(t)$ show that any initial condition such that $H(q_0, p_0) = 0$ with $q_0 < 0$ and $p_0 > 0$ will take an infinite time to reach q^*. Note that such initial conditions correspond to being on a specific branch of the separatrix.

(e) Can you determine how the initial condition in the previous question approaches the fixed point?