Universität of Göttingen
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Methods of Computational Physics
WiSe 2019/20

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Sheet 3: Rare Events

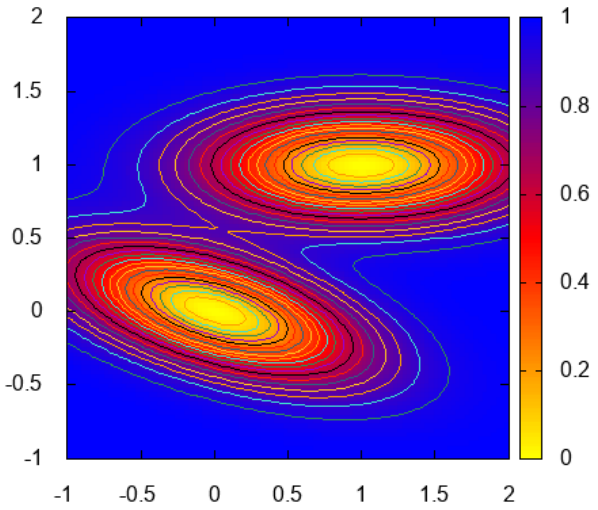
Week 10.12.2019

- **Transitions between two minima**

  Consider a particle in two-dimensional space, $\mathbf{q} \in [-1:2][-1:2] \subset \mathbb{R}^2$, that is subjected to the external potential

  $$V(\mathbf{q}) = V(q_1, q_2) = \left(1 - e^{-(q_1 - 0.3q_2)^2 - 8(0.3q_1 + q_2)^2}\right)\left(1 - e^{-(q_1-1)^2 - 8(q_2-1)^2}\right) \qquad (1)$$

  depicted below. Periodic boundary conditions are applied.



  a) Use **Henkelman's dimer method** to locate the saddle-point of the potential. What is the potential energy at this saddle.

  b) The dynamics of the particle is described by a Monte-Carlo jump process. Implement a Monte-Carlo program that uses uniformly distributed, random displacements within the interval $|\Delta q_\alpha| < 0.3\sqrt{kT}$ with $\alpha = 1, 2$. Compute the **committor probability**, $q_+(\mathbf{q})$, that a trajectory, which starts at $\mathbf{q}$, will first reach the minimum B at $(1, 1)$ rather than the minimum A at $(0, 0)$. How does the committor probability depend on temperature, kT? Use $kT = 0.001$, 0.01 and 0.1. Obtain an approximate for the location of the line, $q_+(\mathbf{q}) = 0.5$.

  c) **flux-over-population method**: Calculate the reactive flux via a steady-state simulation, using the following procedure: Simulate the time evolution of the system via the Monte-Carlo dynamics. Whenever the system reaches the minimum B at $(1, 1)$, delete it and create a new system, whose initial reaction coordinate is chosen according to $p_{\text{birth}}(\mathbf{q}) \propto \exp\left(-\frac{V_{\text{A}}(\mathbf{q})}{kT}\right)$, where $V_{\text{A}}(\mathbf{q}) = V(\mathbf{q})$ if $\mathbf{q}$ is in the basin associated with the local minimum A at $(0, 0)$ and infinite otherwise. The flux j is defined as the number of particles that are shuffled from the basin B $(1, 1)$ to A $(0, 0)$. How does the flux depend on temperature kT?

d) Compute the **Minimum Energy Path (MEP) via the string method**. How does the potential energy vary along the MEP. Visualize the MEP in the energy landscape, $V(q_1, q_2)$. **Bonus:** Given the result of Henkelman's dimer method, is there an easier way to compute the MEP?

e) Use **forward-flux sampling** to obtain the transition rate, k_{AB}. Use the result of task b and/or d to define appropriate interfaces. Compare the result with that of task c. What are the advantages and disadvantages compared to task c?