

Constraining the Semiclassical Initial Value Representation (for applications to molecular clusters)

David W.H. Swenson
W.H. Miller Research Group

19 April 2007

Capturing quantum effects in the dynamics of complex systems is one of the challenges facing modern theoretical chemistry. Purely quantum methods are intractable for large systems, and purely classical dynamics contain no information about quantum effects. Semiclassical methods, however, can approach the feasibility of classical simulations while retaining quantum effects. In particular, the semiclassical initial value representation (SC-IVR) is a valuable technique for adding quantum effects to classical trajectory simulations.¹

In this work, we develop a version of the SC-IVR which allows holonomic (geometric) constraints, such as fixed bond lengths, to be placed on the system being investigated. This will allow us to make the rigid-monomer approximation for molecular clusters. In that approximation, one ignores the high frequency motions associated with the intramolecular vibrations while still capturing the intermolecular motions which allow us to study cluster properties.

The particular variant of the SC-IVR used in this research is the coherent state, or Herman-Kluk (HK) IVR.² It approximates the time evolution operator as

$$e^{-i\hat{H}t/\hbar} \approx (2\pi\hbar)^{-F} \int dq_0 \int dp_0 \mathcal{C}_t(q_0, p_0) |q_t p_t\rangle \langle q_0 p_0| e^{iS_{\text{cl}}(q_0, p_0; t)}$$

where $S_{\text{cl}}(q_0, p_0; t)$ is the action of a classical trajectory evolved for time t from initial coordinates q_0 and initial momenta p_0 , and $\mathcal{C}_t(q_0, p_0)$ is the “HK prefactor,” a complex number which depends on the initial and time-evolved states of the system.

The HK-IVR calculation involves three parts, each of which must be adjusted in order to incorporate constraints:

1. Classical trajectories are calculated to give the action $S_{\text{cl}}(q_0, p_0; t)$ and the time-evolved state $|q_t p_t\rangle$. We can constrain these using either Andersen’s RATTLE algorithm³ or Kneller’s projection method.⁴
2. The HK prefactor, $\mathcal{C}_t(q_0, p_0)$, is constrained using Kneller’s projection method.
3. We constrain the Monte Carlo-selected initial conditions q_0 and p_0 by passing them through a single RATTLE step (following Roy’s previous work⁵ on a constrained IVR).

This technique has been applied to the simple model of a rigid diatom in a one-dimensional harmonic well. In the near future, we will use this technique to predict spectra for molecular clusters, specifically for HCl and for water. More distant future research may involve applications to macromolecules such as proteins, or the implementation of constraints in IVR-based techniques for calculating correlation functions.

¹(a) W.H. Miller. *J. Phys. Chem. A* **105**, 2942 (2001) (b) W.H. Miller. *Proc. Nat. Acad. Sci.* **102**, 6660 (2005) (c) W.H. Miller. *J. Chem. Phys.* **125**, 132305 (2006).

²M.F. Herman and E. Kluk. *Chem. Phys.* **91**, 27 (1984).

³H.C. Andersen. *J. Comp. Phys.* **52**, 24 (1983).

⁴G.R. Kneller. *J. Chem. Phys.* **125**, 114107 (2006).

⁵B.B. Harland and P.-N. Roy. *J. Chem. Phys.* **118**, 4791 (2003).