

# Sampling the Wigner Distribution Obtained from Correlated Vibrational Wave Functions

**Robert Cvjetinović, Mihael Eraković, Nađa Došlić and Marin Sapunar**

*rcvjetin@irb.hr*

*Division of Physical Chemistry, Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia*

Without a sufficiently accurate representation of the initial phase space distribution, subsequent surface hopping simulations won't yield meaningful results [1, 2]. Sampling from the harmonic Wigner distribution is a popular choice since it is a computationally cheap way to account for zero-point energy that works reasonably well for rigid systems. However, it often fails to properly describe large amplitude motion. In the case of methylhydroperoxide, this leads to a qualitatively wrong distribution of products in subsequent surface hopping simulations [1, 2]. We recently proposed a sampling procedure using the Wigner distribution obtained from a vibrational self-consistent field (VSCF) wave function, and found that it was able to mitigate this error. Since the anharmonicity is treated in a mean-field manner, it remains very efficient compared to other sampling procedures [2]. However, neglecting the explicit vibrational correlation could also lead to qualitatively wrong results.

In this work, we investigate the Wigner distributions obtained from the correlated vibrational wave functions of two systems. The first is a model sombrero potential for which the VSCF calculation using linear coordinates does not converge. However, even a relatively low number of products of linear basis functions can properly describe the curved motion. The second system is methylhydroperoxide, whose VSCF Wigner distribution was found to be reasonable, but not quantitatively correct [2]. The problem that arises when one includes correlation is that both the time to sample the  $2N$  dimensional phase space and to evaluate the Wigner distribution at a single point increases rapidly with the size of the system. To remedy this problem, we treat the system within the vibrational active space self-consistent field framework, where the molecule is partitioned into active modes, for which the correlation is treated explicitly, and bath modes, which are treated in a mean field manner [3]. The modes which should be grouped together in the active subspace(s) can be identified from the initial VSCF calculation. The results obtained indicate that the method could be applied to large systems with strongly correlated modes while remaining computationally inexpensive.

## References:

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