The vMCG Method: Complete Simulations of Non-Adiabatic Dynamics using a Gaussian Wavepacket Basis

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Propagating a multi-dimensional wavepacket using the time-dependent Schrödinger Equation is a computationally hard problem that scales exponentially with the number of degrees of freedom in the system. In contrast to the traditional grid-based approach, one way to ease the scaling is to describe the evolving wavepacket by a superposition of Gaussian functions, often referred to as Gaussian Wavepackets (GWPs). There are a variety of algorithms for the propagation of the GWPs that provide the time-dependent basis set. All have advantages and disadvantages, but most use classical trajectories which leads to good scaling, but poor convergence and problems in dealing with quantum phenomena such as tunneling. There is also the problem in selecting the initial functions.

One method that promises to overcome the convergence and initial selection problem is the variational Multiconfigurational Gaussian Wavepacket (vMCG) method. Based on the MCTDH wavepacket propagation method, it variationally couples the evolving basis functions as well as the expansion coefficients, and as the result the functions follow "quantum trajectories" [1]. While suffering from the usual numerical problems of GWPs caused by the non-orthonormal basis set, the method has been shown to perform well using analytical potentials describing non-adiabatic phenomena [2].

In addition, like all GWP methods, vMCG can be used with on-the-fly potential energy surfaces provided by quantum chemistry prograns [3,4]. This saves the effort of pre-calculating surfaces and allows complete flexibility in the molecular evolution. A recent *propagation diabatisation* procedure allows the complete treatment of non-adiabatic systems [5], limited only by the quality of the electronic structure calculations.

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