Numerical Integration of Quantum Dynamics in the Floating Multiple Gaussians Basis

Kazeev N.A., Morozov I.V., Valuev I.A.

Joint Institute for High Temperatures of RAS, Moscow, Russia

The Floating Multiple Gaussians Basis [1] is an effective basis for expansion of the trial wave function for the numerical quantum dynamics. For example, in the Split Wave Packets Molecular Dynamics method [2] single electron wave functions are expanded in a set of Gaussian wave packets (WP) ϕ_k. The Gaussians are called floating because their parameters (positions, momenta, etc.) are treated as dynamical variables. A trial many-body wave function is then constructed depending on the quantum approximation for electron spins, for example in the simplest Hartree case it reads: $\Psi_h(\{\mathbf{x}_k\},t) = \prod_k \phi_k(\mathbf{x}_k,t)$.

The trial wave function is substituted into the time dependent Schroedinger equation and the resulting equations of motion follow from the variational principle [3]:

$$\frac{dq_i}{dt} = \sum_j (\mathbf{N}^{-1})_{ij} \frac{\partial H}{\partial q_j}, \tag{1}$$

where **q** is the complete set of all dynamical variables of all WPs, $N_{ij} = -2\hbar \,\mathrm{Im}\left\langle \frac{\partial \Psi}{\partial q_i} \middle| \frac{\partial \Psi}{\partial q_j} \right\rangle$ is the norm matrix and *H* is the quantum expectation value of the energy for a given trial wave function. For the Gaussian basis the elements of the norm matrix may be obtained analytically, however inversion of the matrix is required at every time step of the numerical integration.

Numerical solution of equations (1) requires special consideration because the norm matrix may become degenerate. This degeneracy is a consequence of the general overcompleteness of the Gaussian basis, so even starting from the initial state with a nondegenerate norm matrix, the degeneracy may appear in the course of the system dynamics. We show that these degeneracy states are attractive for the dynamical system and thus constitute a serious problem when solving the dynamics numerically. Physically the degeneracy in the norm matrix is an indication of the linear dependence in the parameter set in a specific system state.

In the present work a method of dynamical treatment of the Gaussain degenerate states is proposed. The method is based on reducing the dimension of the parameter set representing the many body wave function when the norm matrix is close to degeneracy. The reduction of the parameter set is achieved by analyzing eigenspectrum of the norm matrix and introducing additional constraints to the system dynamics, which correspond to the eigenvectors with small eigen numbers. The constraints are introduced temporarily and conserve the total energy and the wave function norm. The method of dynamical constraints is applied together with the variable time stepping procedure to control the application and release of the constraints.

In this contribution we describe the method of dynamical constraints and its application to the Split WPMD simulations in detail. We implement the constrained norm matrix method within the variable time stepping scheme for the fourth order Runge-Kutta integrator. We analyze the effect of the constraints on the solution of the dynamical quantum systems. We show that the parameters of the method may be chosen so that the constraints do not influence the physical characteristics of the system such as quantum expectation values of particle coordinates, energies and quantum state populations.

References

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