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Multi-State Non-Adiabatic Direct-Dynamics on Propagated Diabatic Potential Energy Surfaces

Gareth W. Richings¹, Graham A. Worth^{2,*}

School of Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK

Abstract

An extension of a recent diabatisation scheme for use in direct-dynamics variational multi-configuration Gaussian (DD-vMCG) quantum dynamics calculations is presented which allows the treatment of systems with more than two electronic states. Methodological updates to the DD-vMCG implementation are presented along with applications of the method to 2-, 3- and 4-state models of the butatriene cation. As a demonstration of the utility of the method, results of 3-state, full-dimensional calculations on the DNA base, thymine, are included, showing the energy dissipation through wavefunction population transfer between states.

Keywords: Direct-dynamics, Diabatisation, vMCG, Thymine

2010 MSC: 00-01, 99-00

1. Introduction

The methods of quantum nuclear dynamics are important in the study of energy dissipation in molecular systems of interest in chemistry and biology. Over the past decade they have shown particular utility in studying photo-excited molecular dynamics and unravelling the results of pulsed laser femtochemistry experiments. Recent examples of joint experimental and quantum dynamics studies from our group include the photochemistry of benzene [1] and pyrrole [2]. The use of such methods by the non-specialist has, however been restricted historically with the main stumbling block being the construction of the potential energy surfaces (PESs) over which the nuclear wavepacket moves. In order to overcome this difficulty

much recent work has focused on the development of direct-dynamics (DD) methods where the PESs are constructed concurrent with the dynamics[3, 4]. Methods such as trajectory surface hopping[5, 6, 7] and *ab initio* multiple spawning[8, 9, 10] have proved their usefulness in many studies. Surface hopping, however, is a semi-classical method and in spawning the basis functions follow classical trajectories which means quantum effects may be hard to describe accurately. The inclusion of quantum mechanical effects in the basis functions can be achieved by use of the variational multi-configuration Gaussian (vMCG) method and its DD variant, DD-vMCG[11, 12, 13, 14, 15, 16, 17, 18, 19, 20].

After photo-excitation, energy dissipation can occur through transfer of wavepacket density

*Corresponding author

Email address: g.a.worth@uc1.ac.uk (Graham A. Worth)

¹Current address: Department of Chemistry, University of Warwick, Coventry, CV4 7AL

²Current address: Department of Chemistry, University College London, Gordon Street, London, WC1H 0AJ

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