On the systematic construction of vibronic coupling Hamiltonians

Harald Solheim,[1] Attila Papp,[2] Clemens Woywod,[1] and Kenneth Ruud[1]

[1]*Theoretical Chemistry (CTCC), Chemistry Department, University of Tromsø, N-9037 Tromsø*

[2]*Department of Theoretical Physics, University of Debrecen,*

H-4010 Debrecen, PO Box 5, Hungary

Abstract

Vibronic coupling phenomena are playing an important role in molecular spectroscopy. This leads to a considerable interest in the development of quantum-mechanical and mixed quantum-classical methods for the treatment of nonadiabatic processes. Information on the dependence of the energies of the relevant adiabatic electronic states on the nuclear coordinates represents a key component for the construction of any Hamiltonian for the description of vibronic coupling dynamics. We will focus in particular on two aspects that are important for the derivation of accurate approximations of the potential energy surfaces with *ab initio* electronic structure methods: (i) The consistency of the approach with respect to the determination of normal coordinates and of excited state energies. (ii) We investigate the effects of neglecting or taking into account the curvilinear nature of normal coordinates on the parametrization of the potential energy functions. The system at the center of this study is the "hydrogen atom of vibronic coupling theory": pyrazine. More specifically, we are interested in the vibronic interaction between the S_1 and S_2 states of this molecule.