

DIABATIC AND ADIABATIC REPRESENTATIONS FOR NUCLEAR MOTION CALCULATIONS OF DIATOMIC MOLECULES

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Traditionally, the (stationary) Schrödinger equation for atomistic systems is solved using the adiabatic approach and associated adiabatic approximation. In cases when interactions between electronic states become important, the associated non-adiabatic effects are taken into account via the first-order and second-order derivative couplings (DDRs) $\langle \psi_{el,i}^a | d/dR | \psi_{el,j}^a \rangle$ (also known as non-adiabatic couplings or NAC) and $\langle \psi_{el,i}^a | d^2/dR^2 | \psi_{el,j}^a \rangle$, respectively. For the diatomic case, the corresponding potential energy curves (PECs) in the adiabatic representation are characterised by avoided crossings. The alternative to the adiabatic approach is the diabatic representation, obtained via a unitary transformation of the adiabatic states by reducing the DDRs as much as possible. For diatomics, the diabatic representation has zero DDR and non-diagonal diabatic coupling (DC) ensued. The two representations are fully equivalent and so should be the rovibronic energies and wavefunctions, resulted from the solution of the Schrödinger equation in the corresponding approximation.

We demonstrate (for the first time), the numerical equivalence between the adiabatic and diabatic rovibronic calculations of diatomic molecules, using *ab initio* curves of yttrium oxide (YO)¹ and carbon mono-hydride (CH)² as examples of two-state systems, where YO is characterised by a strong NAC, while CH has a strong diabatic coupling. Rovibronic energies and wavefunctions are computed using a new diabatic module implemented in our variational rovibronic code DUO³. We show that both the first and second order DDRs are important to include, with the second DDR arguably even more important than the first order DDR. We also show that there is no one choice of representation to be used within nuclear motion calculations, where the convergence of the vibronic energies can strongly depend on the representation used.

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³[10.1016/j.cpc.2015.12.021](https://doi.org/10.1016/j.cpc.2015.12.021) S.N. Yurchenko, L. Lodi, J. Tennyson, and A.V. Stolyarov, Duo: A general program for calculating spectra of diatomic molecules, *Comput. Phys. Commun.*, **202**, 262 (2016)

