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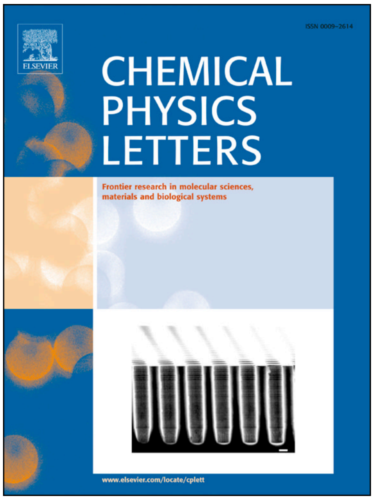

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Energy-switching potential energy surface for ground-state C_3

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Abstract

The multiple energy switching scheme [J. Chem. Phys. 119 (2003) 2596] has been used to improve the double many-body expansion (DMBE II) potential energy surface of C_3 near its linear global minima by morphing it with an accurate Taylor-series expansion [J. Chem. Phys. 144 (2016) 044307]. The final ES form attains the accuracy of the local form in reproducing the rovibrational spectrum of C_3 while keeping unaltered all key attributes of the original DMBE II, namely conical intersection seams and dissociative channels. The ES form is therefore commended for adiabatic spectroscopic and reaction dynamics studies.

Keywords: C_3, potential energy surfaces, energy switching, rovibrational spectroscopy

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1. Introduction

In principle, a global potential energy surface (PES) is expected to reproduce experimental data at regions of the nuclear configuration space where such information is available, and behave in a physically reasonable manner elsewhere (namely, at intermediate and long-range regions) [1–4]. In practice, such a requirement is seldom fulfilled. Despite all recent computational/methodological developments, the above problem still poses a challenge to both *ab initio* theory and analytical modeling [5], particularly if aiming at spectroscopic accuracy [6–21] (the list is by no means complete, with references to other work being obtainable by cross-referencing).

This led one of us [6] to suggest a simple, yet reliable, scheme in which two potential forms [$V_1(\mathbf{R})$ and $V_2(\mathbf{R})$] optimal at distinct energy regimes can be merged together and switched smoothly from one to the other as a function of energy such that the final energy switching (ES) form is accurate everywhere [6, 7, 9, 14]. As usual, $V_1(\mathbf{R})$ is a double many-body expansion (DMBE)-type [4, 22] function or any global form that warrants a realistic description of the whole surface including the location and well depth of the potential minimum(a). In turn, $V_2(\mathbf{R})$ is a local-type form that attains spectroscopic accuracy near such minimum(a). The ES potential ($V_{\rm ES}$) is then given by [6]

$$V_{\rm ES} = f(\Delta E)V_1(\mathbf{R}) + [1 - f(\Delta E)]V_2(\mathbf{R}), \qquad (1)$$

with

$$f(\Delta E) = \frac{1}{2}\left\{1 + \tanh[(\gamma_0 + \gamma_1 \Delta E^m)\Delta E]\right\}, \qquad (2)$$

where $\Delta E = E - E_0$ is the displacement from some reference energy E_0 at which $V_1(\mathbf{R})$ and $V_2(\mathbf{R})$ are equally reliable, and $f(\Delta E)$ is a switching function that ensures $V_{\rm ES} \equiv V_2(\mathbf{R})$ for large negative energy displacements (at the absolute minimum) and $V_{\rm ES} \equiv V_1(\mathbf{R})$ for large positive ones (at the atom-diatom dissociation limits). In turn, γ_i $(i = 0, 1)$ are disposable parameters to be optimized for a selected even power of m [6]. Clearly, $V_{\rm ES}$ benefits from the advantages of both individual forms, while avoiding their limitations [6, 7, 9]. The ES scheme has proved effective in obtaining spectroscopically accurate global PESs for H_2O [6, 7, 9, 17], H_3^+ [8, 11] and also for systems such as ArHCN [23], HO_3 [24] and HeHCN [25].

Recently, Varandas suggested further refinements onto the approach by introducing the multiple ES (MES) scheme [14]. The novel methodology is particularly useful to convey spectroscopic accuracy for systems in which the switching from $V_2(\mathbf{R})$ to $V_1(\mathbf{R})$ takes place in a narrow energy window, as is the case for $NO_2(1^2A')$ [14]. Accordingly, the ES potential ($V'_{\rm ES}$) assumes the form [14]

$$V'_{\rm ES} = f'_i \dots f'_3 f'_2 f'_1 \left[V_1(\mathbf{R}) - V_2(\mathbf{R})\right] + V_2(\mathbf{R}), \qquad (3)$$

with the switching functions f'_i being defined by [14]

$$f'_i(\Delta E') = \begin{cases} \exp\left[-\beta_i \left(\frac{\Delta E'_0}{\Delta E' + \xi} - 1\right)^{n_i}\right] & \text{if } \Delta E' < \Delta E'_0 \\ 1 & \text{if } \Delta E' \geq \Delta E'_0. \end{cases} \qquad (4)$$

In the above equation, $\Delta E' = E - E_{\rm min}$ is the energy displacement with respect to the absolute minimum of the global PES, while $\Delta E'_0 = E'_0 - E_{\rm min}$ measures the energy difference between $E_{\rm min}$ and some cutoff energy E'_0 [14]. Typically, E'_0 can be judiciously chosen in such a way as to keep unaltered some chosen topographical feature of $V_1(\mathbf{R})$ (*e.g.*, a conical intersection [14]) or simply represent the energy threshold at which the Taylor-series-expansion-type form $V_2(\mathbf{R})$ is valid. In turn, β_i is a trial-and-error

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