# REGULAR ARTICLE

# Five New Ab initio Potential Energy Surfaces for the

# O($^3P$, $^1D$) + H$_2$ System

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**Abstract:** Five new potential energy surfaces ($1^{1,3}$A', $2^1$A', $1^{1,3}$A'') for O ($^3P$, $^1D$) + H$_2$ system have been constructed. The *ab intio* single-point energies were calculated for 11060 geometries using five-state state-averaged complete active space self-consistent field (SA-CASSCF) and Davidson corrected multireference configuration interaction method (MRCI+Q) with aug-cc-pVQZ basis sets. A back–propagation neural network (NN) is utilized to fit the potential energy surfaces. The fitted potential surfaces and some important crossings among them are presented. Adiabatic quantum scattering calculations with total angular momentum $J = 0$ are carried out on the new potential surfaces and compared with the results based on previous surfaces.

## 1 Introduction

Reaction of O with H$_2$ has been the project of study for many years. This reaction has generated considerable interest for a variety of nonadiabatic phenomenon: nonadiabatic transition of singlet states [1-3], spin-orbit induced triplet-singlet transition [4] and transition

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in exit-channel region for studying multiplet branching between OH($X^2\Pi$) multiplet levels [5]. Thus, several potential energy surfaces [1,6,7,8,9] have been developed to study adiabatic and nonadiabatic reaction dynamics.

There are eight potential energy surfaces (PESs) accessible to reactants O ($^3P$, $^1D$) + $H_2$: 1-3$^1$A', 1, 2$^1$A'', 1, 2$^3$A', 1$^3$A'. Four states (1$^{1,3}$A', 1$^{1,3}$A'') of them correspond to ground products H + OH ($X^2\Pi$), 2$^1$A' correlates with excited products H + OH($A^2\Sigma$), and the other three excited states(3$^1$A', 2$^1$A'', 2$^3$A'') are repulsive and correlate with upper excited products. High-quality PESs have been obtained for ground state 1$^1$A'[7-9]. Dobbyn and Knowles [1] have constructed DK PESs of singlet states (1,2$^1$A', 1$^1$A'') along with electrostatic coupling between 1$^1$A' and 2$^1$A'. And many nonadiabatic dynamics calculations have been carried out on DK PESs [2,3,10,11]. The above singlet PES 1$^1$A', and triplet PESs 1$^3$A'', 1$^3$A' of Rogers *et al.*[6] were used to study spin-orbit induced transition [12-14]. There is no degeneracy in asymptote OH-H region of the above triplet states, where switching function was used to correct this inadequacy. Recently, Alexander *et al.*[5] have carried out *ab initio* calculations for the four states (1$^{1,3}$A', 1$^{1,3}$A'') in product region to study multiplet branching in O($^1D$) + $H_2$ reaction. Nonadiabatic reaction dynamics requires accurate representations of the *ab initio* PESs involved in reaction. The energy intervals among the coupling PESs and locations of crossing seams have a big effect on transition probabilities, which should be determined accurately. There is a clearly need for removing unnecessary error from different *ab initio* method and fitting procedures for PESs involved in those nonadiabatic dynamics. For this reason, in this paper new high-quality potential surfaces were constructed employing a SA-CASSCF/MRCI+Q scheme with the same weight given to all of the states in state-average procedure.

In this work, we developed five global potential surfaces (1, 2$^1$A', 1$^1$A'', 1$^3$A'' and 1$^3$A') correlate with reactants O($^3P$, $^1D$) + $H_2$ and products H + OH($X^2\Pi$, $A^2\Sigma$). The PESs are directly constructed by *ab initio* energies without considering spin-orbit and electrostatic coupling. The paper is organized as follows. In the next section, *ab initio* molecular electronic structure theory is outlined with stationary point properties for the states, and the fitting procedure of PESs is presented in detail. In Section 3, several features of the surfaces are discussed. Conclusions are given in Section 4.

## 2 Methods

The energies for all data points were calculated using multi-reference configuration interaction (MRCI) scheme with Dunning's aug-cc-pVQZ atomic orbital basis set [15]. Multireference Davidson correction was included to account for the effect of higher-order