Beyond Born-Oppenheimer Constructed Diabatic Potential Energy Surfaces for HeH_2^+

Koushik Naskar[1], Satyam Ravi[1,2], Satrajit Adhikari[1,*], Michael Baer[3] and Narayanasami Sathyamurthy[4]

[1]*School of Chemical Sciences, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, West Bengal, India*

[2]*School of Advanced Sciences and Languages, VIT Bhopal University, Bhopal, 466114, India*

[3]*The Fritz Haber Center for Molecular Dynamics, The Hebrew University of Jerusalem, Israel*

[4]*Indian Institute of Science Education and Research Mohali, SAS Nagar, Manauli 140306, India*

[*]Email: *pcsa@iacs.res.in*

First principles based beyond Born-Oppenheimer theory [1] has been employed to construct multi-state global Potential-Energy Surfaces (PESs) for the HeH_2^+ [2-7] system by explicitly incorporating the Nonadiabatic Coupling Terms (NACTs). Adiabatic PESs and NACTs for the lowest four electronic states ($1^2A'$, $2^2A'$, $3^2A'$ and $4^2A'$) are evaluated as functions of hyperangles for a grid of fixed values of the hyperradius in hyperspherical coordinates. [7] Conical intersection between different states are validated by integrating the NACTs along appropriately chosen contours. Subsequently, adiabatic-to-diabatic (ADT) [8] transformation angles are determined by solving the ADT equations to construct the diabatic potential matrix for the HeH_2^+ system [7] which are smooth, single-valued, continuous, and symmetric and are suitable for performing accurate scattering calculations for the titled system.

References:

[1] B. Mukherjee, K. Naskar, S. Mukherjee, S. Ghosh, T. Sahoo and S. Adhikari, *Int. Rev. Phys. Chem.* **38**, 287 (2019).

[2] W. A. Chupka and M.E. Russell *J. Chem. Phys.* **49,** 5426 **(**1968).

[3] R. Güsten, H. Wiesemeyer, D. Neufeld, K. M. Menten, U. U. Graf, K. Jacobs, B. Klein, O. Ricken, C. Risacher and J. Stutzki, *Nature* **568,** 357 **(**2019).

[4] T. Joseph and N. Sathyamurthy, *J. Chem. Phys.* **80**, 5332 (1984).

[5] C. N. Ramachandran, D. De Fazio, S. Cavalli, F. Tarantelli and V. Aquilanti, *Chem. Phys. Lett.* **469,** 26 (2009).

[6] X. N. Tang, H. Xu, T. Zhang, Y. Hou, C. Chang, C. Y. Ng, Y. Chiu, R. A. Dressler, and D. J. Levandier, *J. Chem. Phys.* **122,** 164301 (2005).

[7] K. Naskar, S. Ravi, S. Adhikari, M. Baer and N. Sathyamurthy, *J. Phys. Chem. A* (2023), doi: https://doi.org/10.1021/acs.jpca.3c01047.

[8] K. Naskar, S. Mukherjee, B. Mukherjee, S. Ravi, S. Mukherjee, S. Sardar and S. Adhikari, *J. Chem. Theory Comput.* **16**, 1666 (2020).