

Geometric Phase Effect in Non-Hermitian Theories

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Understanding the spectroscopy of many Jahn-Teller systems necessitates the correct treatment of conical intersections and their associated geometric phase effect, $E \otimes e$ Jahn-Teller systems being a prominent example [1]. It has been well-established that the topography around conical intersections between excited electronic states is incorrectly described by coupled cluster [2] and many other single reference theories: the intersections are “defective”. In coupled cluster theory, this is because the description of electronic same-symmetry degeneracies is flawed and has a number of well-known non-physical artifacts [3,4] that can only be fully removed by modifying the standard coupled cluster equations [5,6]. In spite of this, we show both analytically and numerically that the geometric phase effect is correctly reproduced upon traversing a path around a defective excited-state conical intersection in coupled cluster theory.

The theoretical analysis is carried out by using a non-Hermitian generalization of the linear vibronic coupling approach. Interestingly, the approach qualitatively explains the characteristic (incorrect) shape of the defective intersections and intersection seams. Moreover, the validity of the approach, and the presence of the geometric phase effect, indicates that defective conical intersections are local (and not global) artifacts. This implies that a sufficiently accurate coupled cluster method could predict nuclear dynamics including geometric phase effects as long as the nuclear wave packet never gets too close to the conical intersections.

[1] T. Weike; D. M. G. Williams; A. Viel; W. Eisfeld; *J. Comp. Phys.* **151**, 074302 (2019).

[2] F. Plasser; R. Crespo-Otero; M. Pederzoli; J. Pittner; H. Lischka; M. Barbatti; *J. Chem. Theory Comput.* **10**, 1395 (2014).

[3] C. Hättig; *Advances in quantum chemistry* **50**, 37 (2005).

[4] A. Köhn; A. Tajti; *J. Chem. Phys.* **127**, 044105 (2007).

[5] E. F. Kjørnstad; H. Koch; *J. Phys. Chem. Lett.* **8**, 4801 (2017).

[6] E. F. Kjørnstad; H. Koch; *J. Chem. Theory Comput.* **15**, 5386 (2019).