

# Comment on “Localized and Delocalized States of a Diamine Cation: Resolution of a Controversy”

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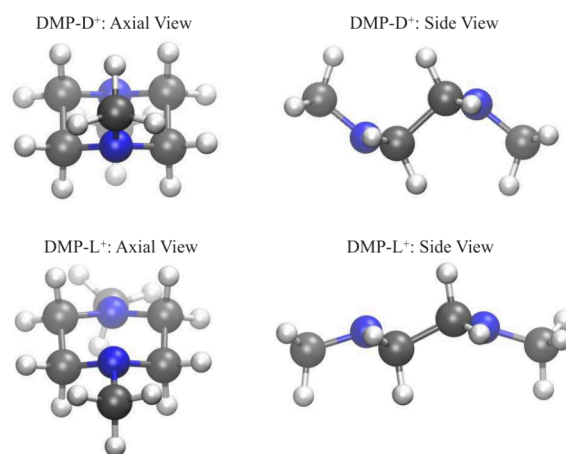
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**ABSTRACT:** Since its appearance in [Cheng, X.; Zhang, Y.; Jónsson, E.; Jónsson, H.; Weber, P. M. *Nat. Commun.* 2016, 7, 11013] and recent re-investigation in [Galyńska, M.; Asgeirsson, V.; Jónsson, H.; Björnsson, R. J. *Phys. Chem. Lett.*, 2021, 12, 1250–1255], the dimethylpiperazine cation (DMP<sup>+</sup>) has generated considerable discussion and controversy in the scientific literature over the existence of stable, local energy minima in this molecular system. Specifically, prior assumptions that the Rydberg state and radical cation of DMP are similar have led to significant confusion and debate regarding the accuracy of various quantum chemistry methods and the existence of stable configurations of DMP<sup>+</sup> itself. The purpose of this Viewpoint is to highlight recent studies that call into question the main findings in the previously mentioned works as well as present new CCSDT (Coupled-Cluster with Single, Double, and Triple excitations) calculations to finally bring closure to this controversy.

Quantum chemists are continuously inspired and challenged by unique chemical systems that test the applicability and limits of their predictive methods. One such example is the radical cation of *N,N'*-dimethylpiperazine (DMP<sup>+</sup>), which garnered significant controversy in a 2016 *Nat. Commun.* paper<sup>1</sup> and was revisited in a recent 2021 *J. Phys. Chem. Lett.* article.<sup>2</sup> In this Viewpoint, we highlight recent work by Kaupp and co-workers<sup>3</sup> that calls into question the main findings in refs. 1 and 2 as well as present new CCSDT (Coupled-Cluster with Single, Double, and Triple excitations) results to finally bring closure to this controversy.

We first give a brief overview of previous experimental and theoretical work on DMP<sup>+</sup> before presenting our new CCSDT calculations. In 1998, Wilbrandt and co-workers carried out a joint spectroscopic and computational study of DMP<sup>+</sup> which showed good agreement between theory and experiment on vibrational intensities and Raman spectra.<sup>4</sup> They attributed the delocalized charge of the ground state to “through- $\sigma$ -bond interaction between the formal lone pair on one amino nitrogen and the odd electron.” Weber and co-workers investigated the Rydberg states of DMP in 2013 and observed an equilibrium between charged-localized and charge-delocalized conformers on the 3s Rydberg potential energy surface (PES).<sup>5</sup> In 2016, Weber and co-workers investigated DMP using wavelength-dependent Rydberg electron-binding energy spectroscopy and time-resolved photoelectron spectroscopy to detect Rydberg states and the cation.<sup>1</sup> From their spectroscopic measurements, the authors concluded that DMP<sup>+</sup> exists as two radical cation conformers, a charge-delocalized dimethylpiperazine (DMP-D<sup>+</sup>) structure and a charge-localized dimethylpiperazine (DMP-L<sup>+</sup>) structure, which correspond to the global minimum and a local minimum, respectively, on the ground-state potential energy surface (PES); see Figure 1. To support their experimental studies, Weber and co-workers carried out theoretical calculations of DMP-D<sup>+</sup>, DMP-L<sup>+</sup>, and its transition state using a Perdew–Zunger Self-Interaction Correction (PZ-SIC)<sup>6</sup> and several density functional theory



**Figure 1.** Axial (left column) and side (right column) views of CCSD-optimized structures of (a) DMP-D<sup>+</sup> and (b) DMP-L<sup>+</sup>.

(DFT) methods, including B3LYP,<sup>7,8</sup> PBE0,<sup>9,10</sup> BHandHLYP,<sup>11</sup> M06,<sup>12</sup> M06-2X,<sup>12</sup> and M06-HF.<sup>13,14</sup> Except for BHandHLYP, Weber and co-workers found that all DFT methods failed to produce a DMP-L<sup>+</sup> minima and, therefore, concluded (surprisingly) that “all DFT functionals commonly used today, including hybrid functionals with exact exchange, fail to predict a stable charge-localized state.”<sup>1</sup>

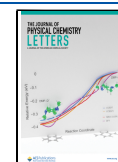
In a follow-up study to ref. 1, our group carried out new, high-quality CCSD-optimized geometries of DMP-D<sup>+</sup>, DMP-L<sup>+</sup> (see Figure 1), and the transition state followed by CCSD(T) and CCSD(T)-F12 single-point energy calculations

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for each of these structures.<sup>15</sup> We also computed a T1 diagnostic and found that none of these stationary points on DMP<sup>+</sup> exhibited any multireference character and, hence, did not require a multireference treatment (additional comments on these calculations are described further below). Most importantly, our study showed that only the CCSD method predicts a barrier (with a small value of 0.1 eV), and DMP<sup>+</sup>, therefore, is not a pathological case for DFT since the high-level CCSD(T) calculations also do not predict a barrier for the DMP<sup>+</sup> system. In response to our CCSD(T) calculations, Weber and co-workers, at the time, could not reconcile the inconsistency between their experiment and our calculations (which did not predict a reaction barrier) and claimed that a multireference treatment was needed for accurate calculations of the DMP<sup>+</sup> system.<sup>16</sup>

In 2021, Bjornsson and co-workers reinvestigated the DMP PES with MRCI+Q (multireference configuration interaction with unlinked quadruples), B3LYP, BHandLYP, CCSD, and CCSD(T) methods.<sup>2</sup> In short, they concluded that DFT and CCSD(T) give qualitatively incorrect barrier heights for the DMP<sup>+</sup> system (because their calculations with these methods did not predict a reaction barrier), whereas their MRCI+Q calculations predict a barrier and, therefore, corroborate the Rydberg experiments of ref. 1.

In the most recent study to date, Kaupp and co-workers revisited the multireference calculations of ref. 2 and carried out new state-averaged multireference (MRCI+Q (SA)) calculations on DMP<sup>+</sup> (additional details on these calculations are described further below) as well as new calculations on the Rydberg states of DMP itself.<sup>3</sup> The Kaupp team found that the energy barrier is an artifact from spatial symmetry breaking in unrestricted Hartree–Fock,<sup>3</sup> which persists in exchange–correlation functionals with a large amount of exact exchange, and CCSD does not fully rectify this problem. Most importantly, Kaupp and co-workers concluded that the original MRCI+Q calculations by Bjornsson and co-workers in ref. 2 “are insufficient to correct the artificial spatial symmetry breaking of the reference wave function.”<sup>3</sup> In contrast, the Kaupp team’s new MRCI+Q (SA) calculations give a barrierless reaction, which further confirms our previous CCSD(T) calculations<sup>15</sup> and analysis that DMP<sup>+</sup> does not require a multireference treatment. In addition, using EOM-CCSD single-point calculations, Kaupp and co-workers found that the Rydberg state is the first excited state of neutral DMP, and the strong binding of the Rydberg electron is responsible for the stable DMP-L<sup>+</sup> Rydberg minimum, which is not present in the cation.<sup>3</sup>

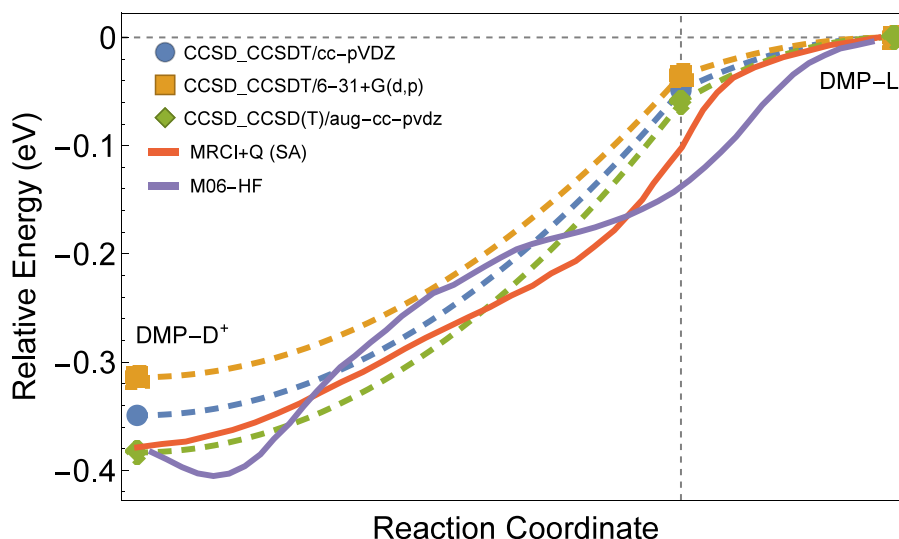
We discuss and clarify two standing issues in this Viewpoint: (1) Can measurements of the DMP<sup>+</sup> Rydberg state (rather than the cation itself) be used to benchmark electronic structure calculations on the cation?, and (2) Which electronic structure methods are correct in predicting whether an energy barrier exists or not in the DMP<sup>+</sup> system?

**(1) Can measurements of the DMP<sup>+</sup> Rydberg state be used to benchmark electronic structure calculations on the cation?** In the original 2016 *Nat. Commun.* paper, Weber and co-workers argued that the “binding energies of the Rydberg states, therefore, yield information about the charge-localized and charge-delocalized cationic states”<sup>1</sup> and support this claim with experimental data that appears to agree with their calculated energies of DMP-D<sup>+</sup> and DMP-L<sup>+</sup>. However, it is important to note that their argument was inferred from time-resolved measurements of the Rydberg state *rather than the*

*ground-state PES of the cation itself*; moreover, there is no evidence that the cation and Rydberg PESs are similar in the DMP system. In addition, Weber and co-workers attribute the lack of vibrational progression in their experiments to support their claim that the potential energy surfaces of the cation and the Rydberg state are similar.<sup>16</sup> While this lack of vibrational progression gives evidence of a similar local curvature between the minima of the cation and Rydberg state, it does not allow for inferences about the energy barrier on the cation PES since the transition state geometry is likely not near the minima. The purported similarity between the cation and Rydberg PESs was directly investigated by Kaupp and co-workers<sup>3</sup> earlier this year, which confirmed that the Rydberg and cation PES are indeed quite different since the former has two stable minima, whereas the latter only has one (see Figure 2 of ref. 3). As such, this recent study clearly shows that the electronic properties of the Rydberg state are unrelated to the cation, and the former should not be used to benchmark quantum calculations for the DMP<sup>+</sup> system.

Prior assumptions that the Rydberg state and cation PES are similar have led to significant confusion and controversy in the scientific literature regarding the accuracy of various quantum chemistry methods, as well as the existence of stable configurations of DMP<sup>+</sup> itself. Bjornsson and co-workers previously claimed that their multireference calculations predict a reaction barrier, which validates the existence of DMP-L<sup>+</sup>, but also note that their argument “hinges on the assumption that the Rydberg states resemble the states of the molecular cation.”<sup>2</sup> However, the extensive calculations by Kaupp and co-workers clearly show that the Rydberg and molecular cation states are qualitatively different, and one final question remains: Regardless of the disconnection between the Rydberg experiment and cation calculations, why do various quantum chemistry methods give different predictions for the DMP<sup>+</sup> system (and which one(s) are correct)? We examine and bring closure to this question in the following sections.

**(2) Which electronic structure methods are correct in predicting whether an energy barrier exists or not in DMP<sup>+</sup>?** Both the Weber and Bjornsson groups claim that the CCSD(T) energies are incorrect because DMP<sup>+</sup> has significant multireference character.<sup>2,16</sup> Our research group originally checked this possibility in 2018 by computing a CCSD T1 diagnostic value of 0.031 (T1 values greater than 0.044 for open-shell systems indicate that a multireference electron correlation method is necessary,<sup>17</sup> although it should be noted that the T2 amplitudes can give a better measure of multireference behavior). In ref. 16, Weber and co-workers mistakenly state that a T1 diagnostic value greater than 0.02 requires a multireference method; however, the 0.02 value is only relevant for closed-shell systems.<sup>18</sup> Furthermore, the Kaupp team commented that the multireference diagnostics from Bjornsson and co-workers “did indeed not strike us as indicative of substantial multi-reference character”<sup>3</sup> and pointed out that the BHandLYP or PZ-SIC result by Weber and co-workers “does not seem to be consistent with appreciable multi-reference character.”<sup>3</sup> As mentioned previously, the Kaupp group thoroughly reinvestigated the multireference calculations of ref. 2 and found that the energy barrier is due to spatial symmetry breaking in the unrestricted Hartree–Fock formalism.<sup>3</sup> As shown in Figure 1 of ref. 3, the Kaupp group found that state-average multireference calculations alleviate this issue and result in a barrierless reaction, in



**Figure 2.** Comparison of various quantum chemistry methods for the potential energy curve between the localized and delocalized state of  $\text{DMP}^+$ . The  $\text{CCSD\_CCSD(T)/aug-cc-pVDZ}$  legend label denotes  $\text{CCSD(T)}$  single-point energy calculations with the  $\text{aug-cc-pVDZ}$  basis set on  $\text{CCSD}$ -optimized structures. The  $\text{CCSD\_CCSDT/cc-pVDZ}$  and  $\text{CCSD\_CCSDT/cc-pVDZ/6-31+G(d,p)}$  legend labels denote  $\text{CCSDT}$  single-point energy calculations with the  $\text{cc-pVDZ}$  and  $6-31+G(d,p)$  basis sets, respectively, on  $\text{CCSD}$ -optimized structures. The  $\text{M06-HF}$ ,  $\text{CCSD(T)}$ , and  $\text{MRCI+Q (SA)}$  data were obtained from refs. 1, 15, and 3, respectively. All of the quantum chemistry methods are in excellent agreement with each other and clearly show the absence of an energy barrier.

agreement with our previous  $\text{CCSD(T)}$  calculations. In particular, the state-average (SA) multireference calculations give a continuous electronic character as a function of the reaction coordinate, whereas the state-specific (SS) calculations produce a discontinuous character and, hence, an artificial energy barrier. In addition, there has been recent work using pair coupled cluster doubles (pCCD) calculations<sup>19</sup> that give results comparable to  $\text{CCSD(T)}$  for  $\text{DMP}^+$ , which further corroborates the PES energetics calculated by the Kaupp<sup>3</sup> and Wong<sup>15</sup> teams.

**New CCSDT Calculations.** Bjornsson and co-workers suggested that “[i]t would be interesting to see whether these problems are resolved at the (very expensive)  $\text{CCSDT}$  (full triples) or  $\text{CCSDT(Q)}$ .”<sup>2</sup> To directly address this open question, we carried out unrestricted single-point  $\text{CCSDT}$  calculations on top of the  $\text{CCSD}$ -optimized geometries from ref. 15 with a  $\text{cc-pVDZ}$  basis set, MP2 natural orbitals, and no symmetry with the MRCC package.<sup>20,21</sup> It is worth noting that the single-point  $\text{CCSDT}$  calculations on the various  $\text{DMP}^+$  structures were indeed extremely computationally intensive, with each  $\text{CCSDT}$  calculation requiring more than 1.3 TB of solid-state disk storage. As such, we slightly lowered the default convergence criteria settings in MRCC, which resulted in negligible differences in the final energy (the change in energy between the last two steps in the  $\text{CCSDT}$  self-consistent loop was  $3 \times 10^{-8}$ ,  $2.21 \times 10^{-6}$ , and  $3.1 \times 10^{-7}$  Hartrees for the  $\text{DMP-D}^+$ ,  $\text{DMP-L}^+$ , and transition state, respectively). In Figure 2, we replot the potential energy curves obtained from  $\text{M06-HF}$ ,<sup>1</sup>  $\text{CCSD(T)}$ ,<sup>15</sup> and  $\text{MRCI+Q (SA)}$ <sup>3</sup> with our new  $\text{CCSDT}$  calculations. The extremely costly  $\text{CCSDT}$  results fully corroborate the barrierless/single stable minimum results of the  $\text{CCSD(T)}$ ,<sup>15</sup>  $\text{MRCI+Q (SA)}$ ,<sup>3</sup> and DFT methods. We also carried out  $\text{CCSDT}$  calculations with a diffuse  $6-31+G(d,p)$  basis set, which also did not predict an energy barrier in the  $\text{DMP}^+$  system. All of the calculated electronic energies in Figure 2 are in excellent agreement with each other and clearly show the absence of an energy barrier since the

energies along the reaction coordinate are all lower than the  $\text{DMP-L}^+$  energy. Collectively, our new  $\text{CCSDT}$  calculations (as well as our original  $\text{CCSD(T)}$  calculations in 2018<sup>15</sup>) clearly demonstrate that the proper inclusion of dynamical correlation effects (i.e., beyond that of  $\text{CCSD}$ ,  $\text{CASSCF}$ , and  $\text{DMRG}$ ) is essential for obtaining accurate energetics for  $\text{DMP}^+$ .

In conclusion, we have presented an overview of past studies on  $\text{DMP}^+$  and provided new  $\text{CCSDT}$  calculations to finally bring closure to this controversy. The thorough study by Kaupp and co-workers earlier this year clearly shows that the electronic properties of the Rydberg state are unrelated to the cation, and the former should not be used to benchmark quantum calculations of the latter for the  $\text{DMP}^+$  system. Moreover, the  $\text{DMP}^+$  system does not require a multireference treatment: conventional  $\text{MRCI+Q}$  calculations give incorrect results and predict an unphysical energy barrier. State-averaged  $\text{MRCI+Q}$  calculations alleviate these problems and predict a barrierless reaction, which is supported by our new  $\text{CCSDT}$  calculations reported in this Viewpoint. While there are certainly cases where a multireference or higher-level treatment is essential for obtaining more accurate results than DFT in pathological chemical systems, the potential energy surface of the diamine cation, unfortunately, is not one of them.

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## Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Cheng, X.; Zhang, Y.; Jónsson, E.; Jónsson, H.; Weber, P. M. Charge localization in a diamine cation provides a test of energy functionals and self-interaction correction. *Nat. Commun.* **2016**, *7*, 11013.
- (2) Galyńska, M.; Ásgeirsson, V.; Jónsson, H.; Björnsson, R. Localized and delocalized states of a diamine cation: Resolution of a controversy. *J. Phys. Chem. Lett.* **2021**, *12*, 1250–1255.
- (3) Reimann, M.; Kirsch, C.; Sebastiani, D.; Kaupp, M. Rydberg electron stabilizes the charge localized state of the diamine cation. *Nat. Commun.* **2024**, *15*, 293.
- (4) Brouwer, A. M.; Zwieter, J. M.; Svendsen, C.; Mortensen, O. S.; Langkilde, F. W.; Wilbrandt, R. Radical cation of N,N-dimethylpiperazine: Dramatic structural effects of orbital interactions through bonds. *J. Am. Chem. Soc.* **1998**, *120*, 3748–3757.
- (5) Deb, S.; Cheng, X.; Weber, P. M. Structural dynamics and charge transfer in electronically excited N,N-dimethylpiperazine. *J. Phys. Chem. Lett.* **2013**, *4*, 2780–2784.
- (6) Perdew, J. P.; Zunger, A. Self-interaction correction to density-functional approximations for many-electron systems. *Phys. Rev. B* **1981**, *23*, 5048–5079.
- (7) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (8) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37*, 785–789.
- (9) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (10) Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **1999**, *110*, 6158–6170.
- (11) Becke, A. D. A new mixing of Hartree–Fock and local density-functional theories. *J. Chem. Phys.* **1993**, *98*, 1372–1377.
- (12) Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, non-covalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215–241.
- (13) Zhao, Y.; Truhlar, D. G. Density functional for spectroscopy: No long-range self-interaction error, good performance for Rydberg and charge-transfer states, and better performance on average than B3LYP for ground states. *J. Phys. Chem. A* **2006**, *110*, 13126–13130.
- (14) Zhao, Y.; Truhlar, D. G. Comparative DFT study of van der Waals complexes: Rare-gas dimers, alkaline-earth dimers, zinc dimer, and zinc-rare-gas dimers. *J. Phys. Chem. A* **2006**, *110*, 5121–5129.
- (15) Ali, Z. A.; Aquino, F. W.; Wong, B. M. The diamine cation is not a chemical example where density functional theory fails. *Nat. Commun.* **2018**, *9*, 4733.
- (16) Cheng, X.; Jónsson, E.; Jónsson, H.; Weber, P. M. Reply to: “The diamine cation is not a chemical example where density functional theory fails. *Nat. Commun.* **2018**, *9*, 5348.
- (17) Rienstra-Kiracofe, J. C.; Allen, W. D.; Schaefer, H. F. The C<sub>2</sub>H<sub>5</sub> + O<sub>2</sub> reaction mechanism: high-level ab initio characterizations. *J. Phys. Chem. A* **2000**, *104*, 9823–9840.
- (18) Lee, T. J.; Taylor, P. R. A diagnostic for determining the quality of single-reference electron correlation methods. *Int. J. Quantum Chem.* **1989**, *36*, 199–207.
- (19) Boguslawski, K. Open-shell extensions to closed-shell pCCD. *Chem. Commun.* **2021**, *57*, 12277–12280.
- (20) Kállay, M.; et al. The MRCC program system: Accurate quantum chemistry from water to proteins. *J. Chem. Phys.* **2020**, *152*, 074107.
- (21) Kállay, M.; Surján, P. R. Higher excitations in coupled-cluster theory. *J. Chem. Phys.* **2001**, *115*, 2945–2954.