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Review article

The unsolved issue with out-of-plane bending frequencies for C═C multiply bonded systems

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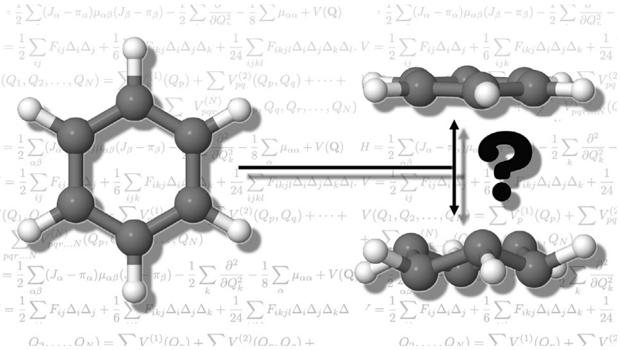
GRAPHICAL ABSTRACT



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ABSTRACT

More than 30 years ago two groups independently identified a problem in the calculation of the out-of-plane bending (OPB) vibrational frequencies for the ethylene molecule using correlated electronic structure methods. Several studies have been done in the meantime to try and understand and resolve this issue. In so doing this problem has been found to be far more insidious than previously realized for acetylene-like and benzene-like molecules, which can become non-linear and non-planar, respectively. The one common feature that all molecules with this problem have is that they contain C═C multiple bonds, and so this has been called the "C═C multiple bond OPB frequency issue" or "the C═C OPB problem." Various explanations for this problem have been advanced such as basis set superposition error, basis set incompleteness error, linear dependences in the basis set, proper balancing of the basis set between saturation and inclusion of higher angular momentum functions, etc. and possible solutions have arisen from these suggestions. All of these proposed solutions, however, amount to one main point connecting them all: modifying the one-particle basis set in some way. None of the explanations that have been advanced, however, really fit all of the data for all of the molecules where this problem has been identified, and importantly, none of these diagnostic tests have been applied to similar molecules where this issue does not appear. In this review, the studies over the last 30 plus years are discussed and relevant data from each of these is compared and contrasted. It is hoped that by collecting and analyzing the data from these studies a path forward to understanding and resolving this issue will become evident.

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Contents

1. Introduction

Over the last 30 years, the field of quantum chemistry has significantly improved its ability to compute accurate and reliable anharmonic rovibrational spectroscopic constants of molecules ranging in size from a few atoms up to approximately 50 atoms. For example, composite schemes have been developed to generate purely *ab initio* quartic force fields (QFFs) or potential energy surfaces (PESs) that will yield B_0 and C_0 rotational constants to ~20 MHz accuracy for molecules with four or more atoms and fundamental vibrational frequencies to within ~6 cm^{-1} [1–4]. These specific composite schemes are limited to 15–20 atoms currently as the base electronic structure method is singles and doubles coupled-cluster theory including a perturbational estimate of connected triple excitations [5–7]. The composite method also includes extrapolation to the one-particle basis set limit and corrections for core-correlation and scalar relativity, and, in some cases, where needed, a correction for higher-order valence correlation. For larger molecular systems, methods have been developed to generate partial QFFs, just the part that is required for second-order vibrational perturbation theory (VPT2) [8,9], using density functional theory (DFT) analytical second derivatives. There are examples where this approach still yields fundamental vibrational frequencies to within ±10 cm^{-1} for certain classes of vibrations such as the C-H stretches in polycyclic aromatic hydrocarbon (PAH) molecules [10–12].

Given the significant progress that has been made, the fact that there remains one problem in computing *ab initio* vibrational harmonic frequencies, or actually even equilibrium geometries, that has eluded a general solution for more than 30 years is somewhat disconcerting. This issue concerns the bending harmonic frequencies, or as implied above in certain cases even the equilibrium geometry, associated with some molecules that contain C═C multiple bonds. The first two papers pointing out this issue were published in the late 1980s, where two groups independently found that the out-of-plane bending (OPB) harmonic frequencies for C_2H_4, ethylene, were found to be too low when using the two configuration self-consistent field configuration interaction (TCSCF-CI) approach [13], or second-order Møller-Plesset perturbation theory (MP2) [14]. In both studies, the harmonic frequency most affected was ω_8 (b_{2g}), although ω_7 (b_{1u}) was also somewhat too low. Both studies also resolved the issue by using larger one-particle basis sets, thus, obtaining harmonic frequencies more in line with the accepted experimental value. It is noteworthy that both of these studies also found that the OPB frequencies were not problematic at the Hartree-Fock level of theory; they only become too low when electron correlation is included via either configuration interaction (CI) or MP2. Many studies have followed these two initial studies and they will be reviewed herein.

This review is structured as follows: Section 2 will describe the nature of the problem with bending vibrational harmonic frequencies, including many studies that have contributed to this field, and the proposed solutions that were tried. Section 3 will discuss all of the possible solutions that have been tried, their similarities and differences, and possible future directions. Section 4 will discuss recent issues with out-of-plane harmonic frequencies for PAH molecules and whether this issue may be related. Section 5 will give concluding remarks.

2. Nature of the problem

2.1. Acetylene-like molecules

Chronologically, the next molecule where this issue arose was in C_2H_2, acetylene, where it was found that the bending harmonic frequencies were too low when computed using MP2, except when *f*-type basis functions were included in the one-particle basis set [15]. Indeed, using an 8s6p3d/6s3p (C/H) basis set the MP2 π_g harmonic frequency was 236 cm^{-1} below the experimental value and the π_u harmonic frequency was 45 cm^{-1} below experiment. Adding an *f*-type basis function to the C atoms yielded a significant improvement to both of the bending harmonic frequencies though the π_g value was still 36 cm^{-1} below experiment, which is 624 cm^{-1}. While it was found that inclusion of the *f*-type basis function to the C atoms increased the Hartree-Fock bending harmonic frequencies, the effect was significantly smaller compared to the MP2 results, and the Hartree-Fock values were always above the experimental values. Thus, the conclusion of this study was that it was necessary to balance the saturation of lower angular momentum basis functions with the inclusion of higher-angular momentum functions. Indeed, soon after the publication of Ref. [15], it was found that one could actually obtain a bent equilibrium structure for C_2H_2 if one just continued to saturate the *spd* C basis set without including higher angular momentum functions [16]. In a 1990 paper that included MP2 harmonic frequencies for the HCCF molecule, it was suggested that this was a general feature of linear molecules and was a result of symmetry [17]. That is, an *spd* basis could be complete for non-linear geometries, but for the linear geometries it was only possible to become complete by including higher-angular momentum functions. Unfortunately, this issue with the bending frequencies of linear molecules has not been reported for systems that do not contain a C═C multiple bond, such as N_2O or CO_2 [18], and the argument also neglects the fact this problem was first identified in the non-linear molecule ethylene.

The work on acetylene was extended [19] in 1998 to the CCSD(T) method (and anharmonic vibrational frequencies), where again the π_g bending harmonic frequency was found to be extremely sensitive to the specific one-particle basis set used. In this study

Dunning's correlation consistent basis sets [20,21] were used, which are designed to balance saturation of low angular momentum basis functions with inclusion of higher angular momentum functions. Moreover, Almlöf and Taylor's atomic natural orbital (ANO) basis sets [22] were also used and these were also designed to balance saturation with inclusion of higher-angular momentum functions, albeit with a much larger primitive basis set relative to the correlation consistent basis sets. The correlation consistent and ANO basis sets minimized the erratic behavior of the bending harmonic frequencies, but they did not eliminate the issue. The ω_4 (π_g) harmonic frequency was still lower than experiment by ~12 cm^{-1} for the aug'-cc-pVQZ and ANO54321 basis sets and ~29 cm^{-1} for the cc-pVQZ basis set. Additionally, the π_g mode still exhibited the largest basis set sensitivity, for example, in moving from the aug'-cc-pVTZ to the aug'-cc-pVQZ basis sets or the ANO4321 to ANO54321 basis sets. The issue of "balance" for acetylene was further exposed when the new composite scheme for computing QFFs [1–3] was used and it was found that the basis set extrapolation procedure was corrupted due to the inconsistent results obtained for the bending harmonic frequencies, especially the π_g mode, across the triple-zeta (TZ), quadruple-zeta (QZ) and 5-zeta (5Z) calculations [23]. In this latter study, one of the CCSD(T)-F12 type methods was used for acetylene as well, specifically CCSD(T)$_{R12}$ [24], and similar to using ANO basis sets, the erratic behavior of the π_g mode harmonic frequency was reduced. However, it was not eliminated when using standard correlation consistent basis sets. When using specialized basis sets designed for the F12 (R12) approach, which include larger primitive basis sets, the erratic behavior for the harmonic frequency was significantly reduced, but, again, not eliminated.

2.2. Benzene-like molecules

The idea of balance was further investigated with Hartree-Fock, MP2, CCSD(T), and DFT calculations on the harmonic vibrational frequencies of benzene [25], C_6H_6, in which various commonly used one-particle basis sets were used, including the ANO basis sets. Again, it was found that the OPB frequencies of benzene were not basis set sensitive at the Hartree-Fock level of theory, but were very sensitive at the MP2 and CCSD(T) levels of theory, and this was especially true for ω_4 (b_{2g}) [25]. Further, it was also noted that the DFT B3LYP functional exhibited essentially no basis set sensitivity for the OPB harmonic frequencies, suggesting that DFT, like Hartree-Fock, was immune to this issue [13–15]. Based upon results from Almlöf and co-workers [16,26] the issue here was suggested to be related to basis set superposition errors (BSSEs), and since ANO basis sets had been demonstrated to possess the smallest BSSEs, the ANO4321 basis set was tried in conjunction with CCSD(T) [25]. It was found that the CCSD(T)/ANO4321 OPB harmonic frequencies then exhibited similar errors to the other harmonic frequencies, essentially correcting the problem here, but we note that a BSSE correction was not performed. The issue was corrected in this case by using an ANO basis set which is designed to minimize BSSE while also maintaining balance between saturation of low-angular momentum basis functions with inclusion of higher-angular momentum basis functions, although it is not clear that this good agreement would be retained if larger ANO basis sets, such as the ANO54321 basis set, are used.

Benzene was further investigated in 2006 when Moran et al. [27] showed that benzene would actually become non-planar at the MP2 and CISD levels of theory with basis sets that were commonly used, including several variants of the popular 6-311G basis set. Moran et al. did not give the exact delineation of the vibrational modes that yielded imaginary frequencies, but they did note these were either of b_{2g} or e_{2u} symmetry, which are the symmetries that Martin et al. [25] found to be problematic in the 1997 study. Hence, these are assumed to be ω_4, (b_{2g}) ω_5 (b_{2g}), and ω_{17} (e_{2u}). Moran et al. employed a diagnostic to determine whether a basis set was subject to this possible erratic behavior for OPB harmonic frequencies termed an intramolecular Basis Set Incompleteness Error (BSIE) [28], which is a two-electron quantity. They noted that only correlated electronic structure methods were subject to this problem, consistent with earlier observations, while Hartree-Fock and DFT were immune since they are fundamentally one-electron theories. Similar to previous studies, their conclusion was that the one-particle basis set needed to have a balance between saturation of the *spd* space and inclusion of higher angular momentum basis functions, especially *f*-type functions. Hence, they recommended use of correlation consistent basis sets or even better ANO basis sets because they minimize BSSE. Finally, Moran et al. also showed this problem extended to a range of other arene type systems including naphthalene and pyridine among others. This is significant because this was the first study to show that the C=C OPB issue extended to larger, less symmetric molecules and ringed compounds that include a heteroatom, namely N.

In 2008, Asturiol et al. [29] investigated benzene again with Hartree-Fock, DFT, MP2, and CISD theories using the 6-31+G*, 6-311G, and 6-311++G basis sets, but they performed counterpoise calculations to correct for intramolecular BSSE. They found that all imaginary harmonic frequencies at the MP2 and CISD levels of theory were corrected (i.e., no longer imaginary), though the variation of the lowest b_{2g} harmonic frequency was still large among the basis sets investigated. Since they did not apply this technique to a series of the correlation consistent basis sets, it is not clear how much erratic behavior would remain amongst the OPB harmonic frequencies. Regarding the Hartree-Fock and DFT calculations, they showed that the counterpoise correction changed the results very little, consistent with earlier observations that these one-electron theories seemed to be immune to the OPB harmonic frequency problem. However, Asturiol et al. did highlight that Jensen [30] had found that the lowest b_{2g} mode in benzene does become imaginary using the BLYP DFT functional with one specific uncontracted augmented (i.e., diffuse functions) *spd* basis set, which is the first indication that perhaps some DFT functionals might exhibit this problem. This will be discussed further below.

Samala and Jordan revisited the MP2 equilibrium geometry and harmonic frequencies of benzene in a 2017 publication wherein they found that a non-planar equilibrium structure was obtained with the aug-cc-pVTZ basis set, or in other words the lowest b_{2g} harmonic frequency for the planar geometry was imaginary [31]. Since the aug-cc-pVDZ equilibrium geometry was planar and the BSSE for the aug-cc-pVDZ basis set should be larger than for the aug-cc-pVTZ basis set, they surmised that the issue was not due to intramolecular BSSE. After examination of the eigenvalues of the overlap matrix, they concluded that the issue was a near-linear dependency in the one-particle basis set. They showed that by "pruning" the basis set of functions with small overlap eigenvalues that the lowest b_{2g} harmonic frequency would become positive again. Additionally, if enough functions were "pruned", then the harmonic frequency would essentially move into alignment with experiment. However, in principle there is nothing wrong with having a basis set with near-linear dependencies. In practice, however, there may be problems because many iterative methods, such as Hartree-Fock or DFT may have difficulties converging because, for example, in a Hartree-Fock calculation the occupation of two or more orbitals that are nearly linearly dependent can keep switching in successive iterations because the energy changes are small and the calculation never converges. However, Jordan has indicated that convergence issues were not an issue [32]. Hence, what Samala and Jordan did, like many previous studies, was to modify the one-particle basis set for a particular case until the harmonic frequencies yielded the desired result. Nonetheless, the findings of Samala and Jordan are significant for two reasons: (1) many earlier studies had suggested that the way to avoid this problem was to use “balanced” basis sets, i.e., basis sets that are balanced between saturation and inclusion of higher angular momentum functions, and the correlation consistent basis sets were designed with this exact concern in mind, and here a series of correlation consistent basis sets exhibited severely erratic behavior, similar to the findings of Huang et al. for acetylene [23]; and (2) secondly, they showed that the problem is not strictly due to intramolecular BSSE.

2.3. Ethylene

As noted in the introduction, ethylene was the first molecule where the issue of OPB harmonic frequencies was first identified [13,14]. Martin et al. reported QFFs computed at the CCSD(T) level of theory with the cc-pVDZ and cc-pVTZ basis sets for ethylene in 1995 [33]. They found that the two OPB frequencies showed the largest basis set sensitivity between the two correlation consistent basis sets, consistent with the earlier studies, though they also state that the erratic behavior of the OPB frequency, especially ω_8 (b_{2g}), is much smaller when using the correlation consistent basis sets. This effect is large enough that the potential error in the OPB fundamental vibrational frequencies may be greater than what would be expected for a high-quality *ab initio* QFF [4,34]. However, it seems that while ethylene was the first molecule for which the OPB issue was found, the effect for ethylene is much smaller compared to either acetylene or benzene. Another recent study [35] gives the harmonic vibrational frequencies for ethylene with many Pople-type basis sets and correlation consistent basis sets. The results are consistent with the studies mentioned above – that ethylene exhibits the C═C OPB problem, but to a much lesser extent than acetylene and benzene. However, the set of harmonic frequencies in Ref. [35] is the most complete. The anharmonic vibrational frequencies were also computed and it is likely that numerical issues in computing the quartic force constants are causing additional problems for the fundamental vibrational frequencies.

3. Discussion

3.1. What we know

The OPB issue for C═C multiply bonded systems appears for *ab initio* correlated wavefunction based methods, while Hartree-Fock seems to be immune. DFT seems to be mostly immune except for the one instance noted above (DFT failures of this nature will be discussed more later). Consequently, this issue appears to be due to one-particle and n-particle basis set coupling, though the exact nature is not known. Several authors have suggested that the cause is due to intramolecular BSSE, though the study by Samala and Jordan, where smaller basis sets which would be expected to have a larger BSSE actually behave better than some larger basis sets, seems to negate that argument. What is consistent with the solutions that all previous studies have found is that by modifying the one-particle basis set in some way, the problem can be minimized and eventually more reasonable OPB harmonic frequencies can be obtained. Means of modifying the basis set include: increasing it in size such as adding an *f*-type function to the C basis; bringing in balance between saturation of the *spd* basis with inclusion of higher angular momentum functions such as the use of correlation consistent or ANO basis sets; including counterpoise corrections; or eliminating some functions through pruning eigenvectors of the overlap matrix. There are two issues with any of these approaches: (1) the effect on the OPB harmonic frequencies is minimized, but not eliminated; and (2) for most of the molecules in these studies, reliable experimental harmonic frequencies were available so that one knew when to stop modifying the one-particle basis set. Consequently, this approach is not conducive to situations where *ab initio* theory is attempting to predict highly accurate fundamental vibrational frequencies of molecules for which no experimental data are available. This also means that while some particular approach may work in minimizing the OPB problem for benzene, it may eventually stop working for larger molecules such as PAHs.

Another piece of the puzzle is that for the most studied molecules, acetylene, ethylene, and benzene, the OPB harmonic frequency that is most affected is always one that retains inversion symmetry. In most cases, the mode that retains inversion symmetry is much more significantly affected than the OPB harmonic frequencies that do not retain inversion symmetry. This is not to say that OPB harmonic frequencies are not affected, because they are. Indeed Moran et al. were able to find basis sets at the MP2 level of theory that yield multiple imaginary frequencies for benzene that included modes which do not retain inversion symmetry. While one particular OPB harmonic frequency is often the most affected, this will ultimately bleed into other vibrational modes of the same symmetry, which several of the benzene studies show [25,27,29,31].

Further, the molecules exhibiting the OPB harmonic frequency issue do not have to be purely hydrocarbon systems. This is shown in the study by Moran et al. where pyridine was found to exhibit the OPB harmonic frequency problem, which is an aromatic ringed system that contains a N in the ring. Thus far, heteroatoms have appeared only in aromatic systems and not in chain like systems, except for HCCF, but in this case F replaces a H atom, not a C atom. However, the fact that the aromatic systems can have any heteroatoms shows that this problem is not strictly linked to the symmetry of the molecule, since the symmetry is significantly reduced, and this also means that inversion symmetry does not need to be a symmetry element of the molecular point group.

This leads to perhaps the most daunting question: why does the OPB harmonic frequency issue not affect all molecules that have a C═C multiple bond? Given the summary of the studies above, one might say that the magnitude of the OPB harmonic frequency issue goes as benzene > acetylene > ethylene. Hence one might expect this issue to arise in a noticeable way for aromatic molecules like c-C_3H_2, cyclopropenylidene, or c-$C_3H_3^+$, its protonated form, as well as l-$C_3H_3^+$, the linear version of the cation that is somewhat analogous to acetylene. (Note: it has been reported that the OPB issue affected c-C_3H_2. However, this was only in the anharmonic correction and it turned out that this was due to a numerical issue in computing the quartic force constants for the out-of-plane modes – see Refs. [36–38].) All of these systems have been studied in detail at the CCSD(T) level of theory in conjunction with correlation consistent basis sets [37,39–41]. Comparison of the CCSD(T) harmonic frequencies across the TZ, QZ, and 5Z basis sets shows that the OPB modes exhibit very little basis set sensitivity, and certainly no more than any of the in-plane vibrational modes. Further, in all three cases, extrapolation to the one-particle basis set limit is unaffected, demonstrating that the C═C OPB frequency issue is not present. In addition, the harmonic vibrational frequencies of cyclic and linear $C_2H_2N^+$ also show no sign whatsoever of the OPB frequency issue [42,43], even though it did appear for pyridine. If BSSE or basis set balance or a basis set incompleteness or a basis set redundancy (as evidenced by small eigenvalues of the overlap matrix) were really the cause of the multiply bonded C═C OPB frequency issue, then one would expect it to appear to some extent in all related or similar systems, and yet this is not the case. There have not been a lot of studies directly aimed at this issue, but they have spanned more than 30 years, and a good explanation for the cause is yet to be found.

3.2. B. The way forward

As indicated above, the fundamental reason for the multiply bonded C═C OPB frequency issue is not known, so a robust strategy to mitigate it is difficult to formulate. Nonetheless, this issue is clearly somehow related to a one- and n-particle basis set coupling, since modification of the one-particle basis set in some way usually allows one to minimize, but not eliminate, the issue. From the studies reviewed above, the approaches which seemed to show the most promise involve the use of contracted basis sets that possess large primitive basis sets, such as the ANO basis sets. This suggest that for molecules like acetylene or benzene, as the molecule moves along the OPB mode coordinates, the basis set requirements change to some extent, similar to what happens in many transition metal diatomic molecules where multiple electronic states of the transition metal atom may be involved moving across the potential energy curve. As a result, one possible solution is to always use ANO basis sets or similar basis sets that have a large primitive set, but of course this can be computationally expensive. It might also be advantageous to make sure that the basis set contraction coefficients are composed of atomic natural orbitals from multiple electronic states weighted properly (i.e., the atomic ground electronic state probably weighted more heavily).

Another possibility is to separate out the OPBs from the other vibrational degrees of freedom and treat them separately, which was done for cyclopropenylidene [44]. As indicated, this particular issue for cyclopropenylidene was found to be related to computing the quartic force constants for the OPBs, but the general approach developed may be useful for systems like acetylene and benzene. Of course, it must be clear that the OPB frequency issue is present before trying this approach. The only way to do that for molecules for which there is no experimental data available is to compute the MP2 or CCSD(T) harmonic frequencies using the TZ, QZ, and 5Z correlation consistent basis sets and examine the basis set sensitivity of the OPB modes, a time-consuming process.

From the perspective of developing an understanding of why the multiply bonded C═C OPB frequency issue arises, one avenue to try would be to use the various diagnostics that have been tried such as BSIE, but such an investigation needs to be performed on systems that exhibit the problem *and* systems that do not in order to determine whether this really is a viable explanation for the problem. In this context, there is another study that explored several metrics for cyclopropenylidene [44], but these metrics were not computed for molecules that clearly exhibit the C═C OPB problem like acetylene and benzene.

4. ***Ab initio*** **and DFT calculations on large PAH molecules**

The multiply bonded C═C OPB frequency issue, as mentioned earlier, only occurs for electron correlation methods, except for the one example found by Jensen [30], and thus the Hartree-Fock and DFT methods are immune from this issue. However, two recent studies that report the harmonic vibrational frequencies of large PAH molecules found that there are many combinations of basis sets and functionals which yield imaginary OPB frequencies, some even at the Hartree-Fock level of theory. In the first, Karadakov [45] studied the harmonic frequencies of the coronene family of molecules $C^{2}_{6n}H_{6n}$ (n = 2–12), which all have D_{6h} symmetry when the molecule is planar. Part of the motivation for the Karadakov study was the fact that two previous studies on coronene had reported imaginary OPB harmonic frequencies using DFT [46,47]. In Karadakov's study, several different basis sets were used in conjunction with several different DFT functionals, including the popular B3LYP, and also the Hartree-Fock and MP2 wavefunction based electronic structure methods. For the smallest coronene, $C_{24}H_{12}$, several different combinations of basis set and method, including HF/TZP and B3LYP/TZP, were found to yield one or more imaginary frequency in OPB-like modes. However, in both of those cases, the imaginary frequency was eliminated by pruning the basis set of just one eigenfunction of the overlap matrix (i.e., removing a linear dependence in the basis set). Examination of Table A1 in Ref. [45] suggest that all of the imaginary OPB harmonic frequencies at the Hartree-Fock level of theory could be related to the need to eliminate linear dependencies in the basis set, but that is not the case for some of the DFT functionals, including the popular B3LYP. There are definitely basis sets where B3LYP yields imaginary vibrational frequencies, though many more basis sets exhibit imaginary vibrational frequencies at the MP2 level of theory. Moreover, in almost all cases, the b_{2g} mode is most affected followed by an e_{2u} mode – the same symmetries and ordering that appear for MP2 calculations on benzene. In most calculations, a single *d*-type polarization function is included on the C atoms and Karadakov finds that the imaginary frequencies can be eliminated with a suitable choice of this exponent in some cases. Thus, Karadakov calls for further development of small basis sets that can be reliably used on large PAH molecules or graphene. Karadakov also studied the singlet and triplet wavefunction stability of the PAHs and found that they were all singlet stable at both the Hartree-Fock and B3LYP levels of theory and were all triplet stable at the B3LYP level of theory.

In the second paper, Bauschlicher [48] studied the harmonic vibrational frequencies of D_{6h} $C_{96}H_{24}$, which is the n = 4 coronene molecule – see the formulae given above from Karadakov, as well as the n = 5 coronene molecule, $C_{150}H_{30}$. Several different basis sets are examined in conjunction with Hartree-Fock and the BP86 and B3LYP DFT functionals. In addition, four different grids were studied ranging from the "ultrafine" and "superfine" grids (as defined in the Gaussian package), as well as two larger grids. The use of 5*d* vs. 6*d* functions (i.e., 5*d* means the 3 *s* component of the *d*-type Cartesian functions has been eliminated) was also studied as well as different values for *d*-type polarization exponents on the C atoms. The first thing to note is that Bauschlicher used the default threshold in Gaussian to eliminate linear dependences in the basis set, and so he did not find any situations where the Hartree-Fock geometries became non-planar. This is consistent with our examination of Table A1 in Ref. [45] where it appears that the imaginary OPB frequencies at the Hartree-Fock level of theory were a result of linear dependencies in the basis set. Bauschlicher found no difference when using 5*d* vs. 6*d* functions, and no differences depending on the choice of grid. These results mean that the planarity of the equilibrium geometry did not depend on these. The basis sets examined were mostly of the Pople variety, such as 4-31G, 6-31G, 6-31G*, etc. but also included the DZ and TZ correlation consistent basis sets as well as some non-standard basis sets (e.g., taking the *sp* functions from one source and the *d* polarization function from a different source). Examining Table 1 of Ref. [48] shows that many of the standard Pople type basis sets yield non-planar geometries, and and the main displacement was stated to be along a b_{2g} mode. Interestingly, at the B3LYP/TZ level of theory, allowing the program to eliminate linearly-dependent functions lowers the symmetry from D_{6h}. Putting these functions back then retained D_{6h} symmetry, which can happen depending on the symmetry of the linearly dependent functions that are removed. Bauschlicher also considered the possibility that different electronic states of the C atom were important at different points along the vibrational modes, and as such he examined the ^3P, ^1D, ^1S, and ^5S states of the C atom but found no obvious issue. The main issue studied in Ref. [45] was changing the 3d exponent for the *d*-type polarization function on the C atoms. An optimal value was found for both $C_{96}H_{24}$ and $C_{150}H_{30}$, but unfortunately, they were not the same optimal value, and in fact the optimal value for $C_{96}H_{24}$ would yield a non-planar $C_{150}H_{30}$.

The primary purpose behind both of these studies was to identify a relatively small basis set that would yield reliable equilibrium geometries and harmonic vibrational frequencies for large PAH molecules, and so their focus was not on addressing the OPB issue generally. Furthermore, it is not entirely clear whether the issues found for various DFT functionals in Refs. [45,48] are related to the multiply bonded C═C OPB frequency issue discussed in most of this review, which is predominantly found with *ab initio* wavefunction methods. In the discussion from Ref. [45], Karadakov seems to imply that indeed these two issues are related, but Bauschlicher does not believe so [48,49]. Nonetheless, with some basis sets, some DFT functionals will exhibit a similar problem with OPB modes for large PAH molecules, and the mode most impacted is again one that retains inversion symmetry.

5. Concluding remarks

In spite of the many impressive achievements that quantum chemists have made in the calculation of vibrational frequencies over the last 30 years, there remains one issue that has not yet been understood or adequately resolved (and frankly has been brushed over). That issue has to do with the out-of-plane bending vibrational frequencies for *some* molecules that contain C═C multiple bonds computed with *ab initio* electron correlation methods. These can exhibit an extreme (acetylene, benzene) or modest (ethylene) basis set sensitivity. In the extreme cases, molecules that are known to be linear can become non-linear (acetylene-like) and molecules that are known to be planar can become non-planar (benzene-like). The OPB mode that is most affected is always one that retains inversion symmetry for molecules that belong to point groups which have inversion symmetry (acetylene, ethylene, benzene). However, at least for aromatic, ringed molecules, the heteroatom N can be present as well (pyridine), showing that inversion symmetry is not necessary. Molecules that have only modest symmetry, like pyridine, also exhibit the C═C OPB problem. Some examples of similar molecules wherein this issue does *not* arise, such as cyclopropenylidene, cyclic and linear $C_3H_3^+$, and cyclic and linear $C_2H_2N^+$, have also been discussed. While many of the studies that have tried to address this problem have attributed the issue to some particular phenomena, such as intramolecular BSSE or BSIE, or linear dependences in the basis set, or having a balanced basis set, none of these explanations fit all of the data. Furthermore, almost none of these types of diagnostics have been studied for both molecules that *do* and *do not* exhibit this problem in order to verify the hypothesis and explain why some molecules exhibit this problem and others do not. By collecting together all of the information from the 30 plus years of studies that have addressed this problem, hopefully, a path forward to better understand and resolve this problem will become evident. The authors have certainly learned quite bit in the preparation of this review, and the hope is that others, who may offer additional possible solutions will as well. Finally, some recent DFT studies on very large PAH molecules are found to exhibit a similar problem for OPB frequencies and equilibrium geometries, but the literature is in conflict as to whether this is related to the C═C OPB frequency issue when computed with *ab initio* electron correlation methods.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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