**Comment on a Spurious Prediction of a Non-Planar Geometry for Benzene
at the MP2 Level of Theory**

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Abstract: MP2 calculations with the full aug-cc-pVTZ basis set give a non-planar structure for benzene. Although this non-physical result can be avoided by using the smaller aug-cc-pVDZ basis set or by scaling or deleting selected functions from the aug-cc-pVTZ basis set, such changes to the basis set can still result in calculated values of the frequencies of the b_{2g} out-of-plane vibrations that are considerably underestimated. The origin of this behavior is traced to linear dependency problems with the aug-cc-pVDZ and aug-cc-pVTZ basis sets when used for benzene.

I. Introduction

In the course of a study of the low-lying temporary anion states of benzene, we had need to calculate the harmonic vibrational frequencies of the neutral molecule, using the MP2 method¹ together with the aug-cc-pVTZ basis set.^{2,3} To our surprise, the calculations on the optimized D_{6h} structure gave an imaginary frequency ($\sim 440i$) for a vibration belonging to the b_{2g} representation. This indicates that at the MP2/aug-cc-pVTZ level of theory the benzene molecule is unstable to distortion to a non-planar D_{3d} structure, which was confirmed by optimizing the geometry in the D_{3d} point group. Our original geometry optimizations and frequency calculations were carried out with density fitting^{4,5} using the Turbomole code⁶ and were duplicated using Molpro,⁷ again employing density fitting. To check whether the density fitting was the source of the problem, we repeated the calculations without density fitting and again found, using both Turbomole and Molpro, that the D_{6h} structure is unstable to out-of-plane distortion to a D_{3d} structure. In contrast with Gaussian 09,⁸ the D_{6h} structure was predicted to be a true minimum at the MP2/aug-cc-pVTZ level, with all frequencies being predicted to be real.

Several years ago, Moran et al.⁹ reported that MP2 and other post-Hartree-Fock wave function calculations with small Pople-type basis sets, *e.g.*, 6-311+G(d)¹⁰, give a non-planar structure for benzene. In that work, the problem was attributed to basis set incompleteness. It was subsequently shown¹¹ that this behavior was a result of internal basis set superposition error (BSSE).¹² However, the problem that we encountered with the MP2/aug-cc-pVTZ calculations on benzene has a different origin than that reported in References 9 and 11 as the molecule was predicted to be planar at the MP2/aug-cc-pVDZ^{2,3} level of theory for which BSSE is larger. In this comment, we identify the cause of the imaginary frequency in the MP2/aug-cc-pVTZ calculations as being due to near linear dependency of the basis set and demonstrate that even with the tightest thresholds generally used for screening for linear dependency and pruning of the basis set, the near linear degeneracy problem remains, causing too low value of the frequencies of the b_{2g} vibrations.

2. Computational Details

The default settings for checking for small eigenvalues of the overlap matrix are 10^{-6} , 10^{-7} , and 10^{-8} with Gaussian 09, Turbomole, and Molpro, respectively. Benzene, as described by the aug-cc-pVTZ basis set, has two eigenvalues of the overlap matrix between 10^{-6} and 10^{-7} and none less than 10^{-7} at its D_{6h} minimum energy structure. The Gaussian code "prunes" the basis set when there are eigenvalues of the overlap matrix smaller than the threshold, and, as a result, when using the default threshold, the calculations carried out using the Gaussian 09 code employed a basis set reduced by two functions. In contrast, the calculations using Molpro and Turbomole necessarily retain the full basis set.

In order to gain additional insight into the nature of the linear dependency problem for benzene, we optimized the geometry and calculated the harmonic frequencies of benzene using the MP2 method under the constraint of D_{6h} symmetry and using different thresholds for the smallest value of the overlap matrix. These calculations, which were carried out using Gaussian 09, reduced the size of the basis set by the number of eigenvalues of the overlap matrix below the specified threshold.

3. Results

Table I reports the harmonic frequencies of b_{2g} symmetry and the energies from MP2 calculations with the full aug-cc-pVTZ basis set as well as with various modifications of this basis set. In the modification denoted aug-cc-pVTZ*, the exponent of the aug- p function of the H atom basis set was scaled by 1.25, and in the one denoted aug-cc-pVTZ**, all aug functions were omitted from the H atom basis set. In addition, results are reported for thresholds of $10^{-7}(0)$, $4 \times 10^{-7}(1)$, $1 \times 10^{-6}(2)$, $2 \times 10^{-6}(3)$, and $1 \times 10^{-5}(11)$ on the eigenvalues of the overlap matrix, where the number of functions removed is indicated in parentheses. When the full aug-cc-pVTZ basis set is retained, the frequency of one b_{2g} vibration is too low by about 26%, and that of the other becomes imaginary. The results are vastly improved with the threshold of 4×10^{-7} for which the basis set is reduced by one function. In this case, the MP2 frequencies for the b_{2g} vibrations being 922 and 465 cm^{-1} compared to the experimental values of 990 and 707 cm^{-1} .¹³ Further significant improvement results from adoption of a threshold of 10^{-6} , with smaller, but non-negligible, further improvements in the values of the calculated frequencies result upon adopting

thresholds of 2×10^{-6} and then 10^{-5} , with the calculated frequencies being within 5 cm^{-1} of the experimental values with the latter threshold.

Table 1. Calculated b_{2g} frequencies (cm^{-1}) of benzene in its optimized D_{6h} structure^a

	Expt. freq.	Basis set							
		aVTZ	aVTZ	aVTZ	aVTZ	aVTZ	aVTZ*	aVTZ**	aVDZ
number of functions deleted		11	3	2	1	0	0	0	0
Smallest retained eigenvalue of overlap matrix		1.3×10^{-5}	2.6×10^{-6}	1.3×10^{-6}	6.7×10^{-7}	3.3×10^{-7}	1.2×10^{-6}	2.2×10^{-6}	2.7×10^{-6}
Energy (a.u.) -231		-0.744339	-0.744648	-0.744662	-0.744676	-0.744683	-0.744834	-0.742320	-0.540220
$\nu(b_{2g}) (\text{cm}^{-1})$	995	998	983	961	922	732	944	983	907
$\nu(b_{2g}) (\text{cm}^{-1})$	703	707	687	634	465	493i	509	656	576

^aThe aug-cc-pVDZ and aug-cc-pVTZ basis sets are denoted by aVDZ and aVTZ, respectively. The aVTZ* basis set differs from the standard aVTZ basis set in that the exponent of the aug p function on the H atoms was multiplied by 1.25, while in the aVTZ** basis set all aug functions were excluded from the H atoms.

In the case of Molpro and Turbomole, the user does not have the option of "pruning" the basis set to reduce linear dependency. Hence, with these codes, the only recourse to reducing the linear dependency is to modify the basis set. However, as seen from Table I, while removing just the aug p functions or all aug functions from the H atom basis set results in a planar structure with all vibrational frequencies real, anomalously low values of the two b_{2g} frequencies result. If one did not know the correct values in advance, one would not realize that the frequencies are underestimated. When the geometry of benzene is re-optimized in D_{3d} symmetry at the MP2 level employing the full aug-cc-pVTZ basis set, the resulting energy is only 6×10^{-6} a.u. lower than that of the D_{6h} structure. In the D_{3d} structure, the C1 and C4 atoms are displaced $\pm 0.009 \text{ \AA}$ relative to the plane of the remaining four carbon atoms.

The five smallest eigenvalues of the overlap matrix for the D_{6h} structure of benzene are of b_{1u} and a_{2g} symmetry. Their numerical values are 3.3×10^{-7} (b_{1u}), 6.7×10^{-7} (a_{2g}), 1.3×10^{-6} (b_{1u}), 2.6×10^{-6} (a_{2g}), and 4.4×10^{-6} (b_{1u}). Thus, using a threshold of 10^{-6} for the smallest eigenvalue of the overlap matrix for the pruning of the basis set results in the reduction by one the number of functions of b_{1u} and of a_{2g} symmetry.

This pruning of the basis set does not impact the energies of the filled Hartree-Fock orbitals, but it does lead to changes in the energies of the virtual orbitals of b_{1u} and a_{2g} symmetry. Table II reports the energies of the lowest energy virtual orbitals of b_{1u} and a_{2g} symmetry obtained from Hartree-Fock calculations retaining all functions as well as from those in which two functions (one each of b_{1u} and a_{2g} symmetry) were removed from the basis set. These changes in the virtual orbitals and their energies are responsible for the small change in the MP2 energy when the basis set is reduced in size.

Table 2. Energies (a.u.) of low-lying virtual orbitals of b_{1u} and a_{2g} symmetry from HF/aug-cc-pVTZ calculations

Orbital symmetry	Threshold on eigenvalues of overlap matrix	
	10^{-6}	10^{-7}
b_{1u}	0.06481	0.06464
b_{1u}	0.15522	0.15474
a_{2g}	0.23378	0.23120

Although our investigation has focused on benzene, exploratory calculations on naphthalene constrained to be planar show that it too has an imaginary vibrational (of a_u symmetry) at the MP2/aug-cc-pVTZ level of theory when the threshold on the eigenvalues of the overlap matrix used for pruning the basis set is 10^{-7} . Thus, we expect that this will be a common problem when applying the MP2 method with such basis sets to polyaromatic hydrocarbons.

4. Conclusions

In summary, MP2 calculations with Dunning-type aug-cc-pVDZ and aug-cc-pVTZ basis sets without pruning of the basis set to reduce near linear dependency do not properly describe the out-of-plane b_{2g} vibrations of benzene. In the case of the aug-cc-pVDZ basis set, the calculated values of the b_{2g} frequencies are much too low, while with the aug-cc-pVTZ basis set, one of the b_{2g} frequencies of the constrained D_{6h} structure, is calculated to be imaginary. The problem is expected to be more serious with

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4 still larger Gaussian-type-orbital basis sets. Some electronic structure codes do not allow for reduction of
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6 the size of the basis set to circumvent this problem, and with programs that do reduce the size of the basis
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8 set to reduce linear dependency, the default threshold may be too small to fully eliminate the problem,
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10 leading to too low frequencies for some out-of-plane vibrations. Although we only considered the MP2
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12 method, these problems are expected to be present with other post-Hartree-Fock methods such as
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14 CCSD.¹⁴ The problems encountered for benzene are expected to occur also in large basis set MP2
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16 calculations on other aromatic systems, and, possibly also, for other classes of molecules.
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