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# $C_8H_8$: A density functional theory study of molecular geometries introducing the localised bond density

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In this paper we use density functional theory with all the common exchange-correlation functionals to investigate the structures of three isomers of $C_8H_8$ found in F. A. Cotton's text, barrelene, cyclooctatetraene, tetramethylenecyclobutane and also ethane and ethene. All calculations were performed with TZ2P basis sets and large quadrature. The results are compared with experiment and those obtained with Hartree–Fock theory. Delocalisation in the three molecules is discussed. A localised bond density is introduced to explain the transferability of the trends in the predictions of the functionals between different molecules. Three-parameter adiabatic connection functionals are examined and their usefulness in geometry prediction questioned. Finally a physical picture of the correlation as modelled by density functional theory is presented and used to explain trends in the overestimation or underestimation of bond lengths.

## 1. Introduction

Within the Born–Oppenheimer approximation, the most difficult part of the electronic Hamiltonian to deal with is the $r_{12}^{-1}$ term which introduces electron correlation. One of the simplest methods of introducing correlation effects is provided by the Kohn–Sham formulation of density functional theory (DFT).[1] This introduces an exchange-correlation potential $v_{xc}$, defined as the functional derivative of the exchange-correlation functional, and in principle local, into a Hartree self-consistent field scheme to handle all the effects of correlation.

The predictive value of DFT is therefore determined by the accuracy of the exchange-correlation functional. As many functionals have only been developed recently, it is important to gain a feel for how different functionals perform for various molecular properties. In this study we examine the relationship between aspects of bond geometry and different functionals. Special note was taken of the different effects of the exchange and correlation parts of the functionals on bond lengths. This is important as a better understanding of how the two parts of the exchange-correlation functional contribute to molecular properties will show the way to better modifications of the functionals. A word should be said about how the molecules were chosen for this study. As a student of chemistry, a text one encounters is '*Chemical Applications of Group Theory*' by F. A. Cotton.[2] This contains Hückel calculations on three challenging isomers of $C_8H_8$: barrelene, tetramethylenecyclobutane and cyclooctatetraene (see Fig. 1–5). Tetramethylenecyclobutane is particularly interesting as although it has been synthesised and shown to be stable[3] it has so far always been omitted from comprehensive high-level calculations on isomers of $C_8H_8$.[4] Geometry optimisations were thus performed on these three isomers and also on ethane and ethene. The predicted geometries were compared with HF-SCF geometries, and for the last two, experimental geometries as well.

In Section 2 we outline the form of the functionals used and our implementation of DFT. In the first half of Section 3, we present our results and in the second half we note some of the interesting trends observed. In Section 4 we introduce the concept of a localised bond density and utilise it to explain some of the properties of functionals. In Section 5, the role of exchange and the 'exact exchange' hybrid functional implementation is examined. In Section 6 the correlation functional is examined and the density functional description of dynamic correlation assessed. Finally in Section 7, we present our conclusions.

## 2. Exchange-correlation functionals

The exchange-correlation functional[5] is defined as the functional relationship between the difference between the energy of a fully interacting system and its non-interacting counterpart and the density of the system, $\rho$. The exchange-correlation potential is the functional derivative as follows:

$$E_{xc}[\rho] = T[\rho] - T^{s}[\rho] + V_{ee}[\rho] - V_{ee}^{s}[\rho] \qquad (1)$$

$$v_{xc} = \frac{\delta E_{xc}}{\delta \rho} \qquad (2)$$

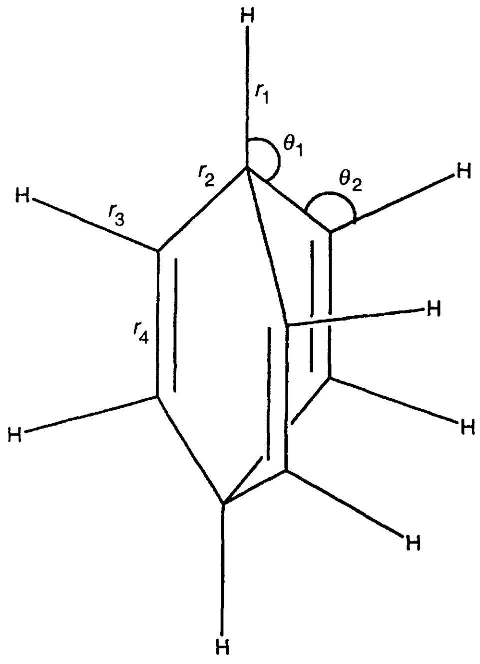

**Fig. 1** Barrelene $C_8H_8$ ($D_{3h}$)

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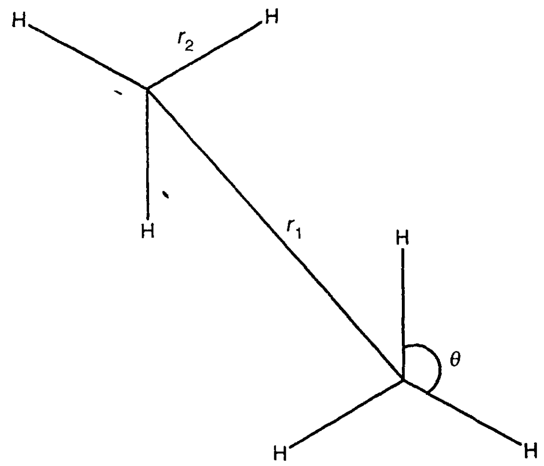

**Fig. 2** Ethane $C_2H_6$ ($D_{3d}$)

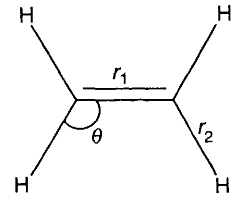

**Fig. 3** Ethene $C_2H_4$ ($D_{2h}$)

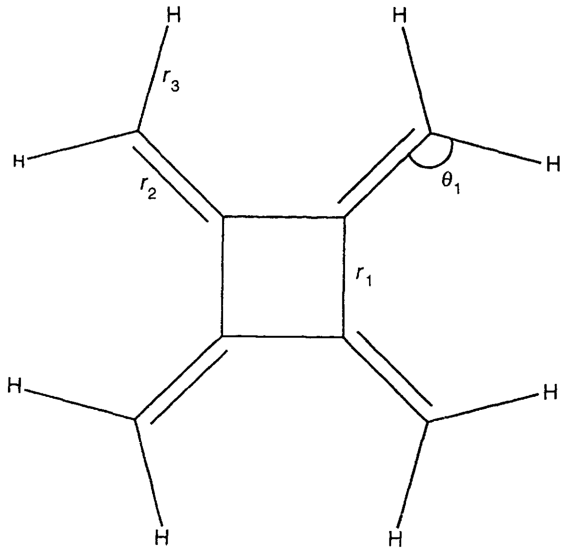

**Fig. 4** Tetramethylenecyclobutane $C_8H_8$ ($D_{4h}$)

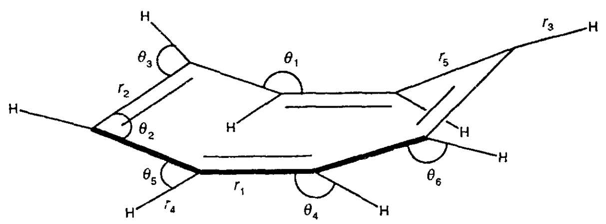

**Fig. 5** Cyclooctatetraene $C_8H_8$ ($D_{2d}$)

The exchange correlation functionals used were LDA, BLYP, BP86, BP91, B3LYP, B3P86 and B3P91.

1. LDA uses the Dirac expression for the exact exchange energy functional for the uniform gas (LDAX),[6] and the Vosko–Wilk–Nusair expression for the correlation energy of the uniform electron gas.[7] Version V, as recommended by the authors, is used. 2. The combination of LDAX and the Becke88 gradient correlation[8] (dependent on $|\nabla\rho|$) is denoted as 'B'. 3. LYP[9] is a correlation functional dependent on $\rho$ and $|\nabla\rho|$, derived from the Colle–Salvetti correlation energy formula.[10,11] 4. P86 and P91 refer to the Perdew86 and the Perdew91[12] correlation functionals. These also include gradient corrections. 5. Functionals that have a '3' in their name are hybrid functionals. These include a small amount of exact exchange, *i.e.*, exchange computed *via* the Hartree–Fock expression for the exchange energy. A three-parameter fit is then employed to mix in this exact exchange with the energy calculated by the original functional.[13]

**Table 1** Optimized geometry of barrelene ($C_8H_8$) in $D_{3h}$ symmetry with HF-SCF and various DFT functionals; bond lengths in angstroms and angles in degrees

| | $r_1^{C-H}$ | $r_2^{C-C}$ | $r_3^{C-H}$ | $r_4^{C=C}$ | $\theta_1$ | $\theta_2$ |
|---|---|---|---|---|---|---|
| SCF(STO-3G) | 1.0868 | 1.5449 | 1.0808 | 1.3085 | 113.17 | 120.53 |
| SCF | 1.0778 | 1.5353 | 1.0713 | 1.3102 | 113.01 | 121.41 |
| LDA | 1.0964 | 1.5204 | 1.0904 | 1.3238 | 113.20 | 121.09 |
| BLYP | 1.0914 | 1.5497 | 1.0852 | 1.3340 | 113.17 | 120.86 |
| BP86 | 1.0934 | 1.5410 | 1.0873 | 1.3328 | 113.16 | 120.98 |
| BP91 | 1.0923 | 1.5403 | 1.0864 | 1.3323 | 113.13 | 120.91 |
| B3LYP | 1.0855 | 1.5386 | 1.0795 | 1.3241 | 113.13 | 121.05 |
| B3P86 | 1.0871 | 1.5322 | 1.0813 | 1.3234 | 113.12 | 121.11 |
| B3P91 | 1.0865 | 1.5318 | 1.0806 | 1.3231 | 113.12 | 121.10 |

The implementation of these functionals and their derivatives in CADPAC[14] is fully described elsewhere.[15] Numerical quadrature was used to evaluate all the integrals employing the Becke partitioning of space,[16] Euler–Maclaurin radial[17] quadrature, and Lebedev angular[18] quadratures. Large quadrature and grid derivatives were used for all the calculations.

## 3. Molecular properties

### 3.1 Optimized geometries

The results of geometry optimization on the four molecules is shown in Tables 1–4. All calculations were performed using a TZ2P Gaussian basis set, unless otherwise stated. Second derivatives for all the molecules were examined and found to be real, indicating the true minimum had been found. In Table 1 we give the geometries for barrelene. Experimental bond lengths were not available for this compound. The CC double bond length was comparable to that of ethene indicating little delocalisation in this compound. This agrees with the conventional organic chemist's view of the compound. The axial CH bonds were longer than the radial CH bonds as expected from simple hybridisation arguments. The CC single bond was somewhat longer than that in ethane, perhaps due to the strain in the bond.

In Table 2 we give the geometries for ethane. B3LYP minimized the average error of the CC and CH bonds ($\Delta r_{\rm rms}$ =

**Table 2** Optimised geometry of ethane ($C_2H_6$) in $D_{3d}$ symmetry with HF-SCF and various DFT functionals; bond lengths in angstroms and angles in degrees

| | $r_1^{C-C}$ | $r_2^{C-H}$ | $\theta_{H-C-H}$ |
|---|---|---|---|
| SCF | 1.5247 | 1.0834 | 107.70 |
| LDA | 1.5100 | 1.1001 | 107.20 |
| BLYP | 1.5401 | 1.0965 | 107.53 |
| BP86 | 1.5315 | 1.0981 | 107.44 |
| BP91 | 1.5314 | 1.0970 | 107.45 |
| B3LYP | 1.5287 | 1.0906 | 107.59 |
| B3P86 | 1.5225 | 1.0918 | 107.49 |
| B3P91 | 1.5225 | 1.0910 | 107.49 |
| exptl.[21] | 1.526 (2) | 1.088 (2) | 107.40 (5) |

**Table 3** Optimised geometry of ethene ($C_2H_4$) in $D_{2h}$ symmetry with HF-SCF and various DFT functionals; bond lengths in angstroms and angles in degrees

| | $r_1^{C=C}$ | $r_2^{C-H}$ | $\theta_{C-C-H}$ |
|---|---|---|---|
| SCF | 1.3144 | 1.0738 | 121.63 |
| LDA | 1.3233 | 1.0934 | 121.65 |
| BLYP | 1.3346 | 1.0882 | 121.77 |
| BP86 | 1.3331 | 1.0903 | 121.72 |
| BP91 | 1.3327 | 1.0894 | 121.73 |
| B3LYP | 1.3253 | 1.0823 | 121.72 |
| B3P86 | 1.3243 | 1.0841 | 121.67 |
| B3P91 | 1.3240 | 1.0834 | 121.69 |
| CCSD(T)[20] | 1.3307 (3) | 1.0809 (3) | 121.44 (3) |

**Table 4** Optimised geometry of tetramethylenecyclobutane ($C_8H_8$ in $D_{4h}$ symmetry with HF-SCF and various DFT functionals; bond lengths in angstroms and angles in degrees

| | $r_1^{C-C}$ | $r_2^{C=C}$ | $r_3^{C-H}$ | $\theta_1$ |
|---|---|---|---|---|
| SCF(6-31G*) | 1.4967 | 1.3189 | 1.0755 | 121.43 |
| SCF(DZP) | 1.4993 | 1.3235 | 1.0760 | 121.25 |
| SCF | 1.4952 | 1.3151 | 1.0730 | 121.34 |
| LDA(6-31G*) | 1.4827 | 1.3374 | 1.0965 | 121.30 |
| LDA(DZP) | 1.3877 | 1.3438 | 1.0974 | 121.09 |
| LDA | 1.4804 | 1.3303 | 1.0929 | 121.20 |
| BLYP(6-31G*) | 1.5044 | 1.3480 | 1.0926 | 121.57 |
| BLYP(DZP) | 1.5097 | 1.3556 | 1.0938 | 121.36 |
| BLYP | 1.5022 | 1.3420 | 1.0874 | 121.49 |
| BP86 | 1.4967 | 1.3408 | 1.0893 | 121.40 |
| BP91 | 1.4964 | 1.3408 | 1.0884 | 121.42 |
| B3LYP(6-31G*) | 1.4964 | 1.3367 | 1.0860 | 121.51 |
| B3LYP(DZP) | 1.5011 | 1.3434 | 1.0872 | 121.29 |
| B3LYP | 1.4938 | 1.3308 | 1.0816 | 121.41 |
| B3P86 | 1.4902 | 1.3302 | 1.0832 | 121.33 |
| B3P91 | 1.4899 | 1.3301 | 1.0824 | 121.36 |

Some calculations were performed using distorted initial geometries, but these found their way back to the $D_{4h}$ symmetry structure.

0.0027 Å), and also gave the closest agreement out of all the functionals for each of the CC ($\Delta r = +0.0027$ Å) and CH ($\Delta r = +0.0026$ Å) bonds. SCF gave a marginally more accurate bond length for the CC ($\Delta r = -0.0013$ Å) bond. Not all bond lengths were predicted to be longer than the SCF bond lengths. For the CC single bond, BLYP, BP86, BP91 and B3LYP predicted bond lengths longer than experiment while SCF, B3P86, B3P91 and LDA predicted bond lengths too short. For the CH single bond all the functionals predicted bond lengths that were too long, the worst bond length being that predicted by LDA. Only SCF underpredicted the bond length.

In Table 3 we give the geometries for ethene. Bond lengths showed reasonable agreement with experiment. BLYP minimised the average error over the CC and CH bonds ($\Delta r_{rms} =$ 0.0037 Å), with BLYP giving the closest agreement for the CC bond ($\Delta r = -0.0039$ Å), and B3P86 giving the best agreement for the CH bond ($\Delta r = -0.0064$ Å). CC bonds were uniformly predicted shorter than experiment, while bonds with all the functionals were predicted to be longer than with SCF. Bond angles were uniformly large, and worse than the SCF bond angle. For the CH bond, LDA, BP86, BP91 and BLYP predicted bond lengths longer than the experimental value, and B3P86, B3P91, B3LYP and SCF predicted bond lengths too short.

In Table 4 we give the geometries for tetramethylenecyclobutane. Experimental bond lengths were not available for this compound. In accordance with simple Hückel theory predictions, the compound is planar which would maximise the 'resonance energy'. CC single bond lengths were shorter than in ethane, and the CC double bond lengths were longer than in ethene, suggesting delocalisation. However, the change in bond lengths of the double and single bonds is of the same order of magnitude as that in butadiene and also in cyclooctatetraene, which is conventionally regarded as non-aromatic. A rigorous study of the delocalisation in butadiene suggests that the change in bond length is due more to changes in hybridisation than due to delocalisation.[19] If we accept this view, we must conclude that there is no delocalisation in tetramethylenecyclobutane, in contrast to what Hückel theory suggests.

In Table 5 we give the geometry of cyclooctatetraene. The molecule is tub shaped (as is known from experiment) as assuming a planar geometry would give too strained a molecule. Although the single and double CC bonds are changed in length with respect to those in ethene and ethane, they are not changed enough to suggest delocalisation. Thus DFT calculations confirm the conventional organic chemist's picture of cyclooctatetraene.

Finally, a note about electronic energies. There has been some discussion in the literature as to the relative stabilities of barrelene and cyclooctatetraene as the energy difference is strongly dependent on the level of correlation used.[4] All our functionals and SCF predict cyclooctatetraene to be more stable than barrelene by a substantial margin ranging from 12.7 kJ mol$^{-1}$ with B3P86 to the large 50.0 kJ mol$^{-1}$ with BLYP. Tetramethylenecyclobutane is less stable than barrelene (24.7 kJ mol$^{-1}$ with BLYP).

## 3.2 Properties of the functionals

The relative ordering of the bond lengths of any specific type of bond, with respect to the different functionals, appears to be transferable between the different molecules.

In the following discussion, where a result was specific to a particular type of molecule, the number of the molecule is given as: 1, barrelene; 2, tetramethylenecyclobutane; 3, cyclooctatetraene; 4, ethene; 5, ethane.

The experimental results are also given in the ordering although clearly they can only be compared with results from

**Table 5** Optimised geometry of cyclooctatetraene ($C_8H_8$) in $D_{2d}$ symmetry with HF-SCF and various DFT functionals

| | $r_1^{C=C}$ | $r_2^{C=C}$ | $r_3^{C-H}$ | $r_4^{C-H}$ | $r_5^{C-C}$ | $\theta_1$ | $\theta_2$ | $\theta_3$ | $\theta_4$ | $\theta_5$ | $\theta_6$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| SCF | 1.3196 | 1.3195 | 1.0764 | 1.0765 | 1.4751 | 127.28 | 127.26 | 117.67 | 117.66 | 114.97 | 114.96 |
| LDA | | | | | | | | | | | |
| BLYP | 1.3471 | 1.3471 | 1.0925 | 1.0925 | 1.4764 | 127.78 | 127.76 | 117.24 | 117.23 | 114.81 | 114.81 |
| BP86 | 1.3456 | 1.3456 | 1.0946 | 1.0946 | 1.4707 | 127.24 | 127.25 | 117.42 | 117.42 | 115.13 | 115.13 |
| BP91 | 1.3451 | 1.3451 | 1.0936 | 1.0936 | 1.4707 | 127.25 | 127.26 | 117.42 | 117.43 | 113.12 | 115.12 |
| B3LYP | 1.3357 | 1.3357 | 1.0861 | 1.0861 | 1.4697 | 127.39 | 127.40 | 117.47 | 117.47 | 114.97 | 114.97 |
| B3P86 | 1.3349 | 1.3349 | 1.0879 | 1.0879 | 1.4657 | 127.11 | 127.08 | 117.50 | 117.49 | 115.24 | 115.23 |
| B3P91 | 1.3346 | 1.3346 | 1.0872 | 1.0872 | 1.4657 | 127.12 | 127.10 | 117.50 | 117.49 | 115.22 | 115.22 |

The geometry could not be converged with LDA; bond lengths in angstroms and angles in degrees.

calculations on the same molecule. In the case of $C_2H_4$ the most reliable structure is probably given by *ab initio* coupled cluster calculations [CCSD(T) with core correlation[20] using spdfg basis sets and extrapolation to infinite basis set limits] and these results are quoted under the heading CCSD(T) in Table 3 in preference to the experimental data. All experimental data is taken from ref. 21.

The observed ordering in all the five types of CH bonds was:

$$r_{\text{LDA}} > r_{\text{BP86}} > r_{\text{BP91}} > r_{\text{BLYP}} \\ > r_{\text{B3P86}} > r_{\text{B3P91}} > r_{\text{B3LYP}} > r_{\text{exptl; 4, 5}} > r_{\text{SCF}} \quad (3)$$

The ordering of the CC single bonds is shown below. While the functionals gave a constant order of relative bond lengths, the SCF bond lengths came in different relative positions: $r_{\text{BLYP}} > r_{\text{BP86}} > r_{\text{BP91}} > r_{\text{SCF; 2}} > r_{\text{B3LYP}} > r_{\text{exptl; 5}} > r_{\text{SCF; 1, 5}} > r_{\text{B3P86}} > r_{\text{B3P91}} > r_{\text{LDA}}$.

Out of all the functionals, B3LYP predicted the most accurate bond length for the CC single bond in ethane, but the SCF bond length was better. Both the LDA and SCF relative bond lengths for CC double bonds varied with the compounds, although the other functionals gave a conserved ordering. The ordering for CC double bonds is: $r_{\text{BLYP}} > r_{\text{BP86}} > r_{\text{BP91}} > r_{\text{exptl; 4}} > r_{\text{B3LYP}} > r_{\text{B3P86}} > r_{\text{LDA; 1, 2}} > r_{\text{B3P91}} > r_{\text{LDA; 4}} > r_{\text{SCF}}$; $r_{\text{BP86}}$ was larger than $r_{\text{BP91}}$ for all the bonds considered. For single bonds the non-LDA, non-hybrid functionals gave bond lengths that were too long, and for double bonds, too short in agreement with other recent DFT calculations.[22] The hybrid functional bond lengths were always shorter than those of their non-hybrid counterparts, and were sometimes longer, sometimes shorter than experiment and sometimes shorter than the SCF bond lengths. LDA gave bond lengths that were often wildly inaccurate, and the sign of the error was not the same for the single bonds C—C (too short) and C—H (too long).

A word about basis sets. The above discussion pertains to calculations using the TZ + 2P basis set. However, a small investigation of basis set dependence was carried out for tetramethylenecyclobutane (see Table 4). It was found that $r_{\text{TZ2P}} < r_{\text{631G*}} < r_{\text{DZP}}$ for all the types of bonds investigated.

## 4. The concept of the localised bond density

### 4.1 Definition

Many of the trends observed were molecule independent but bond dependent. This fits in with the classical concept of the chemical bond as being localised and largely transferable between molecules.[23] In this implementation of DFT the Kohn–Sham orbitals were chosen to diagonalise the K–S operator, and being eigenfunctions of the symmetry operators of the molecules were delocalised. However, density functional theory provides an attractive and intuitive description of localised bonding in terms of a well defined localised bond density.

The electron density for a closed-shell molecule is invariant under a unitary transformation of the orbitals:

$$\rho = 2\sum_{i=0}^{n/2} \phi_i^2 = 2\sum_{i=0}^{n/2} \eta_i^2 \quad (4)$$

where $\eta_i$ are the transformed localised orbitals. By analogy with Hartree–Fock theory, a convenient transformation would be the Edmiston–Ruedenberg transformation,[24] which maximises the self energy of the orbitals, expressed as:

$$J_{\text{self}} = \sum_i \iint |\phi_i(r_1)|^2 \frac{1}{r_{12}} |\phi_i(r_2)|^2 \, \mathrm{d}^3r_1 \, \mathrm{d}^3r_2 \quad (5)$$

Then one has a unique definition of a localised bond density as

$$\rho_i = 2\eta_i^2 \quad (6)$$

which is an attractive definition as unlike the corresponding HF bond density, it is in principle exactly additive, that is the sum of all the localised bond densities will give the true density of the molecule.

### 4.2 Energy minimisation and bond geometries

The central theorem of DFT is that the energy is expressible as a functional of the density

$$E = F[\rho] = F[\rho_i \cdots \rho_n] \quad (7)$$

Within the Born–Oppenheimer approximation the energy depends parametrically on the bond lengths of the molecule. The energy functional is given by

$$E[\rho] = \sum_A \int \rho(r) \frac{Z_A}{|r_A - r|} \, \mathrm{d}^3r + F[\rho] + U_{\text{NN}} \quad (8)$$

where $U_{\text{NN}}$ is the internuclear repulsion. To find the equilibrium geometry one minimises the Lagrangian:

$$L[\rho] = E[\rho] - \mu \int \rho(r) \, \mathrm{d}^3r \quad (9)$$

At equilibrium,

$$\frac{\partial L}{\partial X} = \frac{\partial F[\rho]}{\partial X} + \frac{\partial U_{\text{NN}}}{\partial X} + \frac{\partial}{\partial X} \times \sum_A \int \frac{Z_A \rho(r)}{|r_A - r|} \, \mathrm{d}^3r - \mu \int \frac{\delta\rho}{\delta X} \, \mathrm{d}^3r \quad (10)$$

$$= \frac{\delta F[\rho]}{\delta\rho} \frac{\delta\rho}{\delta X} + \sum_A \int \frac{\partial}{\partial X} \frac{Z_A \rho(r)}{|r_A - r|} \, \mathrm{d}^3r + \frac{\partial U_{\text{NN}}}{\partial X} - \mu \int \frac{\delta\rho}{\delta X} \, \mathrm{d}^3r = 0 \quad (11)$$

where $X$ is a particular bond length, and the dependence of the energy on the orbital coefficients has been eliminated as the density is variationally optimised. $\delta F[\rho]/\delta\rho$ is the functional derivative of the universal energy functional, and is thus molecule independent, although it is dependent on the exchange correlation potential since if one writes the functional form as:

$$F[\rho] = F^{\text{s}}[\rho] + E_{\text{xc}}[\rho] \quad (12)$$

where

$$E_{\text{xc}}[\rho] = \int G(\rho, \nabla\rho, \ldots, ) \, \mathrm{d}^3r \quad (13)$$

then the gradient is:[25,26]

$$\frac{\partial F[\rho]}{\partial X} = \int \frac{\delta G}{\delta\rho} \frac{\delta\rho}{\delta X} \, \mathrm{d}^3r + \frac{\delta F^{\text{s}}}{\delta\rho} \frac{\delta\rho}{\delta X} \\ = \int v_{\text{xc}} \frac{\delta\rho}{\delta X} \, \mathrm{d}^3r + \frac{\delta F^{\text{s}}}{\delta\rho} \frac{\delta\rho}{\delta X} \quad (14)$$

The term $\mathrm{d}U_{\text{NN}}/\mathrm{d}X$ is simply the change in the electrostatic energy of a collection of point charges when the bond distance between two charges is changed, and is, to first order, dependent on the nuclear charges delimiting the bond. The second term will depend on $\delta\rho/\delta X$ and $\sum_A \delta(Z_A/|r_A - r|)/\delta X$. Now introducing localised bond densities,

$$\frac{\delta\rho}{\delta X} = \sum_j \frac{\delta\rho_j}{\delta X} \approx \frac{\delta\rho_i}{\delta X} \tag{15}$$

where $\rho_i$ was defined earlier as the bond density over the bond length X. This means that any term containing the derivative of the density (the first, second and fourth terms) is approximately dependent only on the localised bond density. Lastly, $\delta(Z_A/|r_A - r|)/\delta X$ (summed over all A) depends on only the nuclear charges $A$ and $B$ (the charges of the nuclei delimiting the bond length $X$) as a change in $X$ will change only $r_A$ and $r_B$.

To summarise so far: to first order $dE/dX$ is dependent on the charges of the nuclei delimiting the bond, the bond density between the nuclei $\rho_i$, and the exchange-correlation potential. $\rho_i$ is dependent on $\eta_i$ (6) which is determined by the following equation:

$$F^{\mathrm{KS}}\eta_i = \sum_{j=1}^{n/2} \eta_j \varepsilon_{ji} \tag{16}$$

where

$$F^{\mathrm{KS}} = \left[ -\frac{1}{2}\nabla_1^2 + \int \frac{Z_A \rho_i(r_1)}{|r_A - r_1|}\,\mathrm{d}^3 r_1 + \int \frac{Z_B \rho_i(r_1)}{|r_B - r_1|}\,\mathrm{d}^3 r_1 + \frac{1}{2}\int \frac{\rho_i(r_2)}{r_{12}}\,\mathrm{d}^3 r_1 + v_{\mathrm{xc}} + v_{\mathrm{other}} \right] \tag{17}$$

where $v_{\mathrm{other}}$ is a term consisting of the inter-electron repulsion and the attraction of the localised charge for the nuclei outside the bond and is thus effectively non-local. The nuclear charges of the nuclei delimiting the bond are $z_A$ and $z_B$. The more local the K–S Hamiltonian ($F^{\mathrm{KS}}$), the more the localised bond density remains unchanged between molecules. The $v_{\mathrm{xc}}$ we used in this study were local or largely local. The non-local term is $v_{\mathrm{other}}$, but the change in this term between different molecules is small by chemical intuition and can be regarded as a perturbation in the K–S Hamiltonian. Thus to a first approximation $\rho_i$ is determined by the nuclei delimiting the bond and the exchange correlation functional.

We can now draw the following conclusions. 1, The localised bond density is determined largely by the type of bond being considered, and is thus to a first approximation transferable between molecules. 2, The gradient of the energy with respect to a certain bond length is dependent (to a first approximation) only on the nuclear charges delimiting the bond, the localised bond density over the length $X$, and the exchange-correlation potential used. 3, From 1 and 2, one can explain the observation that trends exist in the relative bond lengths of specific bonds over the range of functionals which are transferable between molecules.

## 5. Exact exchange and hybrid functionals

Exact exchange is defined as:

$$E_x^{\mathrm{exact}} = -\frac{1}{2}\sum_{ij} \iint \phi_i(r_1)\phi_j(r_1) \times \frac{1}{r_{12}}\,\phi_i(r_2)\phi_j(r_2)\,\mathrm{d}^3 r_1\,\mathrm{d}^3 r_2 \tag{18}$$

The basis for the incorporation of exact exchange, into the functionals B3LYP, B3P86 and B3P91 is the adiabatic connection. This gives the exchange correlation energy as a functional of the inter-electronic coupling parameter $\lambda$.[27] For spin-unpolarised systems this is:

$$E_{\mathrm{xc}} = \frac{1}{2}\iint \frac{\rho(r_1)}{r_{12}} \int_0^1 h_{\mathrm{xc}}^{\lambda}(r_1, r_2)\,\mathrm{d}\lambda\,\mathrm{d}^3 r_1\,\mathrm{d}^3 r_2 \tag{19}$$

where $h_{\mathrm{xc}}^{\lambda}$ is the exchange-correlation hole function. The exchange-correlation energy is thus dependent on the interaction of the electron density with the exchange-correlation hole. $\lambda = 0$ represents the non-interacting limit, describing a system with the same density as the fully interacting system, but with no interelectronic repulsion and which has a hole which is the exchange hole of the Slater determinant of Kohn–Sham orbitals, where the energy is given by expression (18). This hole is largely static, and for a two-electron system (*e.g.* the hydrogen molecule) is static.[13,28] Density functional holes on the other hand are localised near each reference point, and thus are a poor representation of the hole in the $\lambda = 0$ limit. The expression for the exchange energy in the hybrid functionals is thus given by the DFT exchange functional, plus a small parametrised amount of the difference between the exact exchange and the DFT exchange energies, in the hope that the exact exchange will give the correct contribution for near $\lambda = 0$ holes. The correlation energy is also scaled, and the parameters (three in all) determined by least-squares fitting to G2 thermochemical data.[13,29]

Noting from earlier arguments that it is fruitful to discuss the variation in predicted bond lengths of a particular bond type with different functionals, how does the incorporation of exact exchange change the bond lengths? Recall that Hartree–Fock predicts bond-lengths shorter than experiment,[30] as the one determinant wavefunction contains the maximum amount of bonding character. The exchange functional deals with exchange and non-dynamic correlation (largely by construction), non-dynamic correlation being defined as that which arises from all configurations which can be constructed from bonding, nonbonding or antibonding valence orbitals. From a quantum-chemical point of view, if we are considering multiple configurations contributing to the wavefunction, the functional does not put enough emphasis on the ground state wavefunction and thus favours a longer bond length than experiment. The exact exchange essentially gives a Hartree–Fock hole, and thus including more exact exchange increases the Hartree–Fock nature of the calculation and results in shorter bond-lengths.

This is what is observed in practice as functionals incorporating exact exchange predict shorter bonds than their non-hybrid counterparts, without fail. However, the hybrid functionals may sometimes predict bond lengths shorter than those of SCF (*e.g.* in CC single bonds). This draws attention to three points.

1. We are reminded that the presence of the correlation functional will mean that replacing the exchange functional with exact exchange will not give the same results as SCF in the limit of 100% exact exchange. As discussed in the next section, correlation can lead to shorter bond lengths. These two reasons explain why it is possible to obtain bond lengths (as in CC bonds) which are shorter than SCF bond lengths.

2. Minimising the energy using conventional variational techniques is known to give the energy to second order, but the wavefunction only to first order. The parameters were determined by least-squares fitting to thermochemical data which included some of the molecules studied such as ethene and ethane. This suggests that with density, as is the case with wavefunctions, thermochemical fitting is a relatively insensitive parametrisation method. To obtain a bond length shorter than the SCF bond length (the worst result obtainable by

'conventional' quantum chemical methods) is clearly poor. This together with lack of theoretical justification for the simple approximation where *a*, *b* and *c* are scaling parameters

$$E_{xc} = E_{xc}^{DFT[scaled(b,c)]} + a(E_X^{Exact} - E_X^{DFT}) \quad (20)$$

clearly limits the predictive value of hybrid functionals where the parameters are pure constants.

3. Exchange functionals overestimate non-dynamic correlation. This is because they do not put enough emphasis on the near $\lambda = 0$ holes where there is no correlation.

## 6. Correlation and higher bond orders

The correlation functional is responsible for dynamic correlation. Dynamic correlation is defined as the correlation introduced by incorporating non-valence orbitals into a CI expansion. The effect of dynamic correlation on bond length is to decrease the bond length,[31] as the electrons can now assume optimum distances from each other in non-valence orbitals, which counters the tendency of non-dynamic correlation to localise the electrons on their individual atoms. It is difficult to separate the effects of exchange and correlation on the bond lengths. This is because of what might loosely be called the relative scaling properties of exchange and correlation. With different types of bonds, the relative importance of exchange and correlation in influencing the equilibrium bond length may change. It is because of these different scaling characteristics that the relative bond length ordering for the functionals is actually specific to bond types and not universal. However, one can tentatively say that P86 tends to introduce less dynamic correlation than P91 as in all the bonds studied, the P86 bond lengths are longer than the P91 bond lengths.

Observed trends are that for single bonds DFT tends to overpredict bond lengths, and that for CC double bonds bond lengths are underpredicted. Other work has shown that for CC triple bonds, bond lengths are even shorter with DFT.[32] We now wish to speculate on the origin of these trends.

It is possible that current functionals overestimate electron–electron dynamic correlation. If one considers non-dynamic correlation, the arguments above involving exact exchange seem to predict that DFT bond lengths not involving exact exchange should always be too long, as no matter the bond type, local functionals of the type considered will always give poor representations of non-localised $\lambda = 0$ limit holes. They will always not include enough Hartree–Fock character, and assuming we had an exact correlation functional, will predict bond lengths too long. This is not true, and indicates not only that our correlation functional is not exact but also that it overestimates correlation as the bond lengths are too short.

A simple physical justification can be provided for this conclusion in the case of LDA. The LDA is based on the uniform density electron gas and is the exact first term in a gradient expansion of $E_{xc}[\rho]$. It evaluates the exchange-correlation energy by means of the approximation

$$E_{xc} = \int \varepsilon_{xc}[\rho(r)]\rho(r)\,d^3r \quad (21)$$

where $\varepsilon_{xc}[\rho(r)]$ is the exchange-correlation energy for a uniform electron gas of the same density as $\rho(r)$. This means that at every point of the integral, the functional is giving the correlation for a gas of uniform density. Physically for the system to contain a central nuclear potential and yet still have uniform density electron gas, the electron–electron correlation must be large and be the dominant potential. Thus correlation is modelled as being far more important than in a true molecular system where the density roughly follows the nuclear potential. At all points in the integral the functional is working from a physical picture which is only valid when correlation is larger than in reality—in a sense the functional is sampling only from a space of all systems with constant density. Thus LDA overestimates correlation effects.

There are some results to support this argument as LDA, which clearly has the largest overestimation of correlation does at times most severely underestimate the bond lengths. More sophisticated functionals are more stable in their predictive power.

However, if overestimating dynamic correlation is linked to an over-uniform (in $\rho$ and also derivatives of $\rho$) model, one may extend this argument to the generalised gradient expansion correlation functionals, where the correlation potential is of the form $v[\rho, \nabla\rho]$. The fact that these functionals depend on the gradient of the density alone and not on higher derivatives means that at each point of the integration the functional neglects inhomogeneities in $\nabla\rho$ cause by higher derivatives, *i.e.* the functional is sampling only from the space of systems with uniform density gradients. This corresponds to an over-uniform correlation model, and thus an overestimation of correlation (though clearly not as poor as in the case of LDA).

This means that if we found the exact generalised gradient expansion, *i.e.* the exact first term in the expansion of $\rho$ containing $|\nabla\rho|$, correlation effects will be overestimated, and including higher term derivatives (assuming they are exact terms) will reduce this overestimation. It is interesting thus to see that this approach to density functional theory (*i.e.* one which models the exchange correlation functional by a gradient expansion in $\rho$) approaches the electron correlation problem from the opposite end to conventional variational wavefunction techniques such as CI, which start off by underestimating correlation.

It is not clear why an overestimation of correlation might be more important in affecting the geometries of higher-order bonds than lower-order bonds. Perhaps in some sense higher-order bonds are more inhomogeneous in the electron density as single bonds are (approximately) axially symmetric. Clearly further work is needed in this area.

## 7. Conclusions

In this study we examined the bond geometries of some organic molecules with all the popular current functionals. The first *ab initio* calculation of the geometry of tetramethylenecyclobutane revealed a molecule without significant delocalisation. The computed geometries of barrelene and cyclooctatetraene confirmed conventional organic chemists' views of the geometries and the delocalisation in these molecules.

It is hoped that the concept of a localised bond density, introduced in this study, should be useful in that it is now possible to talk of how a functional performs for any particular bond. We also looked at the gradient of the energy with respect to bond length and its relation to the exchange correlation potential and the localised bond density. Exact exchange functionals and the role of exchange in predicting bond geometries were examined, and the suitability of simply parametrised hybrid functionals for geometry prediction was questioned. Finally, the role of correlation in bond geometry was discussed, and we suggested that DFT, at least in its gradient expansion formulation, overestimates correlation. Simple physical arguments were put forth to justify this view. The relative importance of exchange and correlation in the prediction of bond geometries of different bonds could not be simply assessed from this study, and clearly more work must be done before this difficult problem can be understood.

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