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ARTICLE *in* CHEMICAL PHYSICS LETTERS · OCTOBER 1999

Impact Factor: 1.9 · DOI: 10.1016/S0009-2614(99)00898-2

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An ab initio study of DNA base pair hydrogen bonding: a comparison of plane-wave versus Gaussian-type function methods

R.S. Fellers [a], D. Barsky [b], F. Gygi [a], M. Colvin [b,*]

[a] *Center for Applied Scientific Computing, Lawrence Livermore National Laboratory, L-415, Livermore, CA 94550, USA*
[b] *Computational Biology Group, Lawrence Livermore National Laboratroy, L-452, Livermore, CA 94550, USA*

Received 28 May 1999; in final form 6 August 1999

Abstract

We have computed ab initio binding energies, optimum geometries, and electrostatic moments for several DNA base pairs by gradient-corrected density functional theory (DFT) using basis sets consisting of plane-wave or Gaussian-type functions. Our findings demonstrate that even with modest periodic cell dimensions and plane-wave cutoff energies, the plane-wave method yields equivalent results to Gaussian basis DFT using very large basis sets and counterpoise corrections.

1. Introduction

The structure and dynamics of DNA has been studied for five decades both by experiment and theory since the discovery of the double helix. Within a DNA double helix, there are a number of intermolecular forces that affect the equilibrium structure, the dynamics of helix formation and distortion, and even the high fidelity of replication. Prominent among these forces are the Watson–Crick hydrogen bonds between the complementary base pairs thymine and adenine (T–A) and guanine and cytosine (G–C) that exist in the DNA double helix (see Fig. 1). These hydrogen bonds have long been assumed to be a necessary component for faithful reproduction of DNA. Recent experiments, however, have called into question the role of these hydrogen bonds in DNA replication [1]. Because of the difficulty in experimentally isolating the effects of distinct intermolecular forces (e.g., hydrogen bonding vs. base stacking interactions vs. solvation effects), computer simulations have played a prominent role in the emerging understanding of DNA biophysics. Notably, there is a substantial body of theoretical work investigating the detailed structures and energetics of nucleotide base pair interactions (see, e.g., Refs. [2–4]).

Chemical simulation methods range from empirical molecular dynamics to ab initio quantum chemistry. Ab initio methods can be extremely accurate, but theories that describe electronic wave functions (e.g., Hartree–Fock and Møller–Plesset theory) have a practical limitation of 50–100 atoms and are not generally viable for dynamical simulations. Additionally, when applied to the study of molecular interactions, such as hydrogen bonding, these methods suffer from an inherent inaccuracy know as the basis set superposition error (BSSE) that arises from

* Corresponding author. Fax: 925-422-2282; e-mail: colvin2@llnl.gov

0009-2614/99/$ - see front matter
PII: S0009-2614(99)00898-2

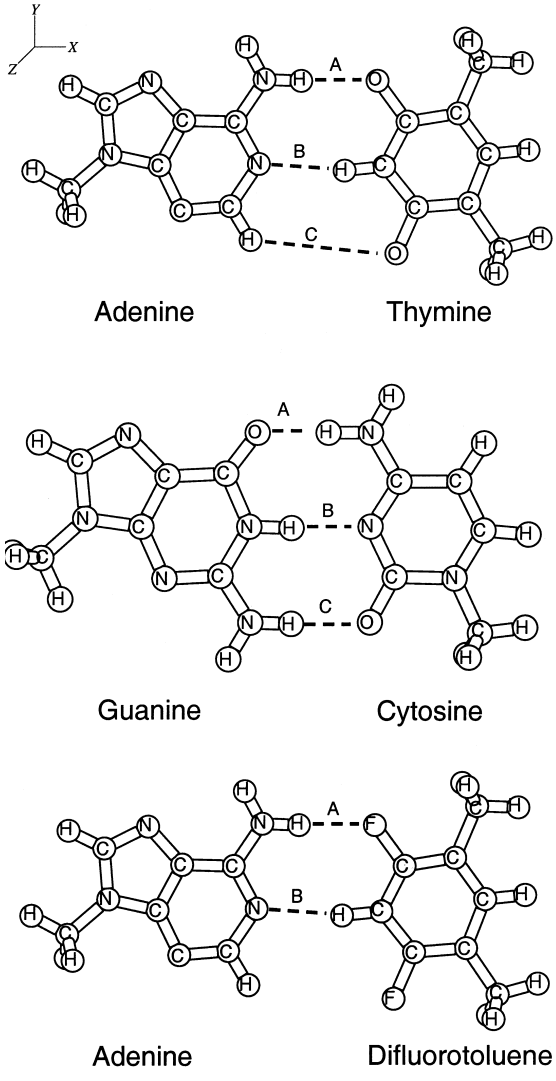

Fig. 1. The three base pairs considered in this study. The cartesian axis define the orientation of the base pairs in the unit cell.

the use of a finite number of atom-centered basis functions. Depending on the size of the basis sets and the level of quantum chemical theory employed, this error can lead to uncertainties as large as the computed interaction energies themselves. A standard way of estimating the BSSE is to compute the Boys–Bernardi counterpoise (CP) correction. Unfortunately, the accuracy of the CP correction itself is not known and therefore does not provide a rigorous upper bound of the error. Some have argued that the CP method overcorrects the interaction energy [5] although there are theoretical arguments that CP correction will produce a rigorously correct energy [6]. Despite this controversy, a number of studies on the prototypical hydrogen bonded system, the water dimer, have shown that CP correction applied to calculations with modest basis sets (e.g., 6-31G(d, p)) yield energies close to predictions from very large basis set calculations (e.g., aug-cc-pV5Z) [7–11], where BSSE becomes vanishingly small, or from BSSE free methods such as the symmetry adapted perturbation theory (SAPT) [12]. In systems of biological interest, where the number of atoms number in the tens or even hundreds (the T–A base pair without sugars contains 36 atoms), computing interaction energies with basis sets large enough to minimize BSSE are impractical. SAPT might become a remedy but its appears to be too demanding for practical consideration; the largest system studied by this method has been the water dimer [12]. Clearly, an efficient method which is inherently devoid of BSSE is desirable.

A quantum chemical method which employs plane waves (PW) rather than Gaussian-type functions (GTF) is such a method. Utilization of a PW basis in density functional theory (DFT) is well established in the field of solid state physics where the natural basis for the electronic states of infinite periodic systems are plane waves. Application of DFT-PW to disordered or isolated systems is relatively new; its beginning can be traced back to the pioneering ab initio molecular dynamics (AIMD) work of Car and Parinello [13] where they illustrated a method of performing MD in a DFT-PW formalism and applied the technique to a Si annealing simulation. Subsequently, the method has been applied to a number of systems in liquid and amorphous solid phases [14] including bulk water [15,16]. For small organic systems, the PW method typically consumes greater computer resources than its GTF counter part. However, due to favorable scaling, the PW method's practical limit is several hundreds of atoms. Because this ab initio method can handle a larger number of atoms, it is now being applied to large systems with biological relevance such as iron–porphyrin [17], proton transfer in gramicidin A [18], retinal dynamics [19], and spin equilibrium of cytochrome P450 [20]. In the past, such systems have only been accesible

through semi-empirical methods such as AM1 or PM3, or through purely classical simulations.

Although the PW method has been applied to several biological systems, the accuracy of the interaction energies computed by this method, especially the non-bonding interactions relevant to DNA such as hydrogen bonding and stacking interactions, have not been well characterized. In a continuing study of DNA base pairing interactions by our group, we carry out GTF and PW calculations for the natural T–A and G–C base pairs as well as the F–A base pair analogue, where F is difluorotoluene, an isostere for T. F has been synthesized to act as a sensitive probe for studying base stacking forces and steric effects because it forms weaker hydrogen bonds with A than does T. F has been shown to be treated like T by DNA polymerase I [1], indicating the importance of steric effects in DNA replication fidelity and contradicting the traditional notion that the high fidelity of nucleotide insertion is primarily due to the presence of strong Watson–Crick hydrogen bonds between the template base and the base being inserted. This has prompted a re-examination of the role of base pair hydrogen bonds [21] and highlights the need for accurate and efficient methods able to characterize the intermolecular forces present in DNA.

2. Computational methods

DFT calculations were performed using the GAUSSIAN 98 set of programs [22] for GTF basis results or JEEP [23] for the PW basis results. In order to make a direct comparison between the two methods, the best gradient corrected functional common to both was used throughout (Becke exchange (B) and Lee, Yang, and Parr correlation (LYP)).

For the GAUSSIAN 98 calculations, geometries are optimized without constraints at the BLYP/6-31G(d, p) and BLYP/6-31 + + G(d, p) levels. BLYP/aug-cc-pVTZ single point energies are computed on BLYP/6-31 + + G(d, p) geometries with the keyword SCF = TIGHT which enforces a convergence of 10^{-8} on the RMS of the density matrix. The CP correction is determined by the method of Boys–Bernardi.

The DFT-PW code employs Hamann pseudopotentials [24] with a cutoff radius $r_c = 1.0$ a.u. for both $l = \mathrm{s}$ and $l = \mathrm{p}$. Although pseudopotentials impose the approximation of frozen atomic core states, they have been shown to be well suited for the study of hydrogen bonded systems such as $(H_2O)_2$ and $(HF)_2$ [25], liquid water under ambient [15,16] and high-pressure, high-temperature conditions [16], and ice [26]. Wavefunctions and geometries are optimized by damped molecular dyamics until the change of the absolute energy was $< 1 \times 10^{-6}$ a.u. which converges the binding energy of the base pairs to better than 0.001 kcal mol^{-1}. Cell dimensions and cutoff energies are noted in the text and in the respective tables. For the 70 Ry cutoff calculations, all monomer and dimer geometries are optimized without constraints. For larger cutoff energies, we have optimized the monomer and dimer structures in $36 \times 36 \times 18$ cells and used these geometries for rigid structure calculations with larger cells. To begin this study we calculated the binding energy of the T–A, G–C, and F–A base pairs using both GTF and PW methods. For the GTF calculations, we performed full geometry optimizations with BLYP/6-31G(d, p) and BLYP/6-31 + + G(d, p), and for the PW calculations we optimized the geometry using a cutoff of 70 Ry and cell dimensions of $36 \times 36 \times 18$ and $40 \times 36 \times 18$. We then chose to carry out an extensive set of calculations on the T–A pair to assess the accuracy and convergence behavior of the PW method.

3. Results

Predicted binding energies, geometries, and electrostatic dipole moments for the T–A, G–C, and F–A base pairs are presented in Tables 1–5. In order to get a rough estimate of the T–A binding energy in the saturated basis set limit, we computed this dimer at the BLYP/6-31G(d, p), BLYP/6-31 + + G(d, p), and BLYP/aug-cc-pVTZ//BLYP/6-31 + + G(d, p) level with CP corrections. In the case of the T–A base pair, these basis sets use 390, 489, and 1131 contracted basis functions, respectively. The binding energies are shown in Table 1 and are plotted in Fig. 2. For comparison, representative high-quality predictions found in the

Table 1
DFT/BLYP binding energies (kcal mol^{-1}) with counterpoise corrections (CPC) for the T–A, F–A, and G–C base pairs as a function of basis set. Geometries were optimized in the 6-31G(d, p) and 6-31 + + G(d, p) calculations. The aug-cc-pVTZ results are rigid structure calculations using the 6-31 + + G(d, p) optimized structure

	T–A	F–A	G–C
6-31G(d, p)	−16.26	−6.41	−29.70
6-31G(d, p) + CPC	−11.28	−2.84	−23.99
6-31 + + G(d, p)	−11.82	−2.89	−24.60
6-31 + + G(d, p) + CPC	−11.11	−2.44	−23.73
aug-cc-pVTZ	−11.24	–	–
aug-cc-pVTZ + CPC	−10.87	–	–

literature are shown in Table 2. As seen in other calculations of weakly bonded systems, there is a large variation of the uncorrected binding energy as a function of basis set (−16.26 kcal mol^{-1} at the 6-31G(d, p) level versus −11.24 kcal mol^{-1} at the aug-cc-pVTZ level). Of particular note is the dramatic change of the uncorrected energy with the inclusion of a relatively small number of diffuse functions (6-31G(d, p) → 6-31 + + G(d, p)), where the binding energy decreases from −16.26 to −11.86 kcal mol^{-1}. The difference between 6-31G(d, p) and 6-31 + + G(d, p) is the addition of diffuse s and p functions on the 2nd-row atoms and the addition of diffuse s functions on the hydrogens. Aug-cc-pVTZ adds diffuse s, p, d, and f functions on the 2nd-row atoms and diffuse s, p, and d functions on the hydrogens. As shown in Fig. 2, CP correction reduces the differences in T–A binding energies between basis sets, however, there remains a 10% difference in this energy upon increasing the basis from 6-31 + + G(d, p) to aug-cc-pVTZ. Comparing the rigid geometry aug-cc-pVTZ results with the smaller basis set results, we estimate the infinite basis set binding energy to be about −10.5 kcal mol^{-1}.

DFT-PW calculations using the same gradient corrected functional for several unit cell sizes and cutoff energies are presented in Table 3 and are summarized in Figs. 2 and 3. With the DFT-PW method, inaccuracies in the computed binding energy are primarily determined by the choice of cutoff energy and unit cell size. The cutoff energy is chosen to be high enough to be able to accommodate the rapid oscillations of the electronic density near the nuclei. For a fixed cell size, the binding energy should approach an asymptotic value as the cutoff is increased. In previous work we found that 70 Ry converges the binding energy of $(H_2O)_2$ and $(HF)_2$ to better than 0.05 kcal mol^{-1} [25].

Since the computation costs of the DFT-PW method scale as $\mathcal{O}(L^3)$ for a fixed number of atoms, where L is the dimension of a unit cell, we wish to use the smallest cell possible. The minimum size of the cell, for the purpose of studying isolated species, must satisfy the requirement that the charge density be vanishingly small at the periodic boundaries. The longest distance between nuclei in the T–A base pair is ∼25 a.u. We found that a $36 \times 36 \times 18$ a.u. cell is large enough to accomodate this requirement. Beyond this minimum cell size, we must also consider the effect of long-range electrostatic interactions between mirror images of the base pairs which will offset the binding energy and may also distort the equilibrium geometry. Since the base pairs are neutral, the leading term is a dipole–dipole interaction energy which will decay as $1/r^3$, where r is the distance between dipoles. Makov and Payne [27] have shown that with a cubic cell, the electrostatic dipole interactions between mirror images cancel and that the first non-zero energy contribution decays as $1/r^5$, which corresponds to quadrupole–quadrupole interactions. In our study, using cubic cells necessitates a significant amount of vacuum that increases the computational costs dramatically. As a point of reference, the T–A base pair in a $36 \times 36 \times 18$ cell with a 70 Ry cutoff requires nearly 1 Gbyte of RAM

Table 2
Representative counterpoise corrected binding energies (kcal mol^{-1}) predicted by alternative exchange-correlation functionals (B3LYP) or model chemistries (Hartree–Fock and 2nd-order Møller–Plesset theories) [2]. The 6-31G*(0.25) basis set is a modification of the 6-31G* basis set where the exponent on the polarization functions have been changed from the standard value of 0.8 to 0.25

	T–A	G–C
B3LYP/6-31G*(0.25) + CPC	−11.9	−26.5
HF/6-31G*(0.25) + CPC	−9.7	−24.6
MP2/6-31G*(0.25) + CPC	−12.4	−25.8

Table 3
Binding energies (kcal mol^{-1}) for the T–A, F–A, and G–C base pairs as a function of cell dimensions (a.u.). Geometries were optimized in each calculation. The plane-wave cutoff energies are given in parentheses

Cell dimensions	T–A (70 Ry)	T–A (100 Ry)	F–A (70 Ry)	G–C (70 Ry)
$36 \times 36 \times 18$	−10.12	−9.92	−1.36	−22.01
$40 \times 36 \times 18$	−10.28	−10.09	−1.44	−21.53
$40 \times 48 \times 18$	−10.30	–	–	–
$40 \times 36 \times 22$	−10.30	–	–	–
$48 \times 36 \times 18$	−10.48	−10.26	–	–
$58 \times 36 \times 18$	−10.53		–	–

to store the wavefunction. In order to estimate the binding energy in the limit of infinite cell dimensions, we used rectangular cells and varied each dimension to determine the sensitivity of the binding energy. As shown in Table 3, by starting with a $36 \times 36 \times 18$ cell and 70 Ry cutoff and then increasing each dimension by $\sim 10\%$, we found that the binding energy is an order of magnitude more sensitive to the x dimension of the cell as compared to y or z. By elongating the x dimension from 48 to 58 a.u., we see that the change in the binding energy is on the order of < 0.05 kcal mol^{-1}. Extending the x dimension from 36 to 58 a.u., we fit the binding energies computed to a polynomial of the form $E = a + b/x^3 + c/x^5$ to arrive at the energy of $\lim_{x \to \infty} E = -10.60$ kcal mol^{-1}. In this fit, the long-range electrostatic interaction appears to be mix of quadrupole–quadrupole and dipole–dipole. The predicted electrostatic moments of the T–A base pair are $|\mu| = 0.7$ a.u. and $\Theta_{xx} = 45.0$, $\Theta_{yy} = -26.4$, and $\Theta_{zz} = -18.7$ a.u. (70 Ry / $58 \times 36 \times 18$, the origin of the electrostatic moments is defined as the center of nuclear charge of the complex). For cell dimensions in the range of 30–40 a.u., the quadrupole–quadrupole interaction energy is as much as an order of magnitude larger than the dipole–dipole interaction, and at 60 a.u. the two interaction energies are nearly equal.

To gauge the convergence of the binding energy as a function of cutoff energy, we repeated some of the smaller unit cell calculations with a 100 Ry cutoff as shown in Table 3. For the three cell sizes computed, the binding energies are ~ 0.2 kcal mol^{-1} weaker than the 70 Ry calculations. A further increase of the cutoff to 120 Ry resulted in a < 0.01 kcal mol^{-1} change in the binding energy from the 100 Ry results.

The optimized hydrogen bond distances for the three base pairs investigated are reported in Table 4. These geometries were calculated with a cutoff of 70 Ry. We noticed that as we increased the cell dimensions, the hydrogen bond distances hardly varied. We also find that the hydrogen bond lengths of the T–A geometries computed at 100 Ry are also within

Table 4
The T–A, G–C, and F–A hydrogen bond distances (a.u.) as a function of cell dimensions (a.u.) and GAUSSIAN 98 basis set. The hydrogen bond labels, A, B, and C, are defined in Fig. 1. PW geometries were optimized at 70 Ry

Cell dimensions	T–A			G–C			F–A	
	A	*B*	*C*	*A*	*B*	*C*	*A*	*B*
$36 \times 36 \times 18$	3.727	3.534	5.488	3.294	3.609	3.589	4.559	4.209
$40 \times 36 \times 18$	3.719	3.538	5.495	3.297	3.612	3.591	4.544	4.201
$58 \times 36 \times 18$	3.717	3.536	5.493	–	–	–	–	–
GAUSSIAN 98 basis set								
6-31G(d, p)	3.596	3.391	5.314	3.302	3.596	3.601	3.980	4.492
6-31 + + G(d, p)	3.605	3.480	5.472	3.328	3.640	3.615	4.121	4.650

Table 5
Total dipole moments $\left(|\mu| = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2}\right)$ for the individual bases and for the three base pairs. Moments are in atomic units

	PW-70 Ry	PW-100 Ry	6-31G(d, p)	6-31 + + G(d, p)	aug-cc-pVTZ
T	1.89	1.86	1.65	1.92	1.85
A	0.99	0.97	0.99	1.06	1.02
T–A	0.73	0.72	0.56	0.73	0.65
G	2.31	–	2.26	2.81	–
C	2.72	–	2.62	2.47	–
G–C	2.34	–	2.44	2.45	–
F	0.79	–	0.61	0.82	–
F–A	0.49	–	0.56	0.47	–

0.01 a.u. of the 70 Ry results. The geometry differences between the PW and GTF T–A and G–C pairs are also small (~ 0.1 a.u.). The differences of the F–A 'hydrogen bonds' between the two methods are larger, ~ 0.4 a.u., although with the PW optimized geometry, the F $\cdots$ H interaction is longer than the GTF counterpart, whereas the N $\cdots$ H interaction is shortened by a similar amount (see Fig. 1).

The dipole moments for the individual bases and base pairs are given in Table 5. We find that in the PW calculations, the dipole moments of the individual bases as well as the net dipole moment of the base pairs, are not sensitive to the choice of cutoff energy or cell dimensions. In the PW results, the dipole moments are constant to within 0.03 a.u. In the GTF calculations, the variability of the dipole moment as a function of basis set is an order of magnitude larger. As an example, in Table 5 we see that the dipole moment of the T–A base pair varies between 0.56 to 0.73 a.u., depending on the choice

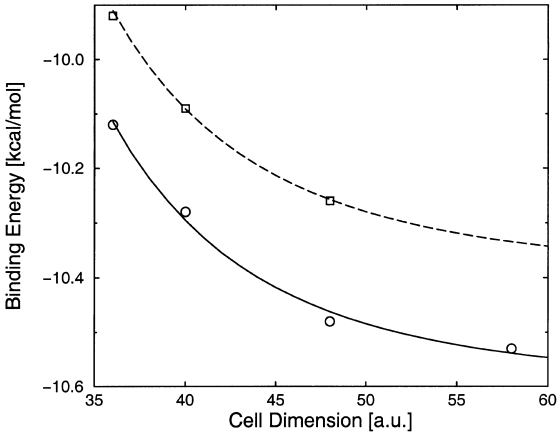

Fig. 2. The convergence of the T–A PW binding energy as a function of cell dimension. The x dimension of the unit cell is varied as the y and z dimensions are fixed to 36 and 18 a.u., respectively. The data points correspond to binding energies computed with cutoff energies of 70 Ry (○) and 100 Ry (□). Binding energies computed at 120 Ry are coincident with the 100 Ry data. The solid line is a fit of the 70 Ry data to a polynomial of the form $E = a + b/x^3 + c/x^5$ which yields $a = -10.60$ kcal mol^{-1}, $b = 6652$ a.u.^{3} kcal mol^{-1}, and $c = 2.100 \times 10^7$ a.u.^{3} kcal mol^{-1}. The dotted line is the same curve shifted by 0.20 kcal mol^{-1} (i.e., $a = -10.40$ kcal mol^{-1}).

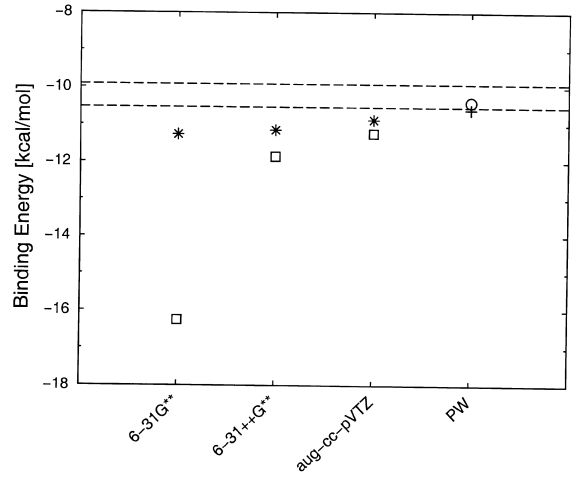

Fig. 3. Shown are the T–A binding energies computed for three different basis set sizes with (∗) and without (□) counterpoise corrections. Also shown are the energies extrapolated to infinite cell dimensions: -10.60 kcal mol^{-1} at 70 Ry (+) and -10.40 kcal mol^{-1} at 100 Ry (○). The dashed denote the total range of DFT-PW energies we have computed (from -9.92 kcal mol^{-1} at 120 Ry / $36 \times 36 \times 18$ to -10.53 kcal mol^{-1} at 70 Ry / $58 \times 36 \times 18$), demonstrating the small spread of binding energies found over a large range of cutoff energies and cell dimensions.

of GTF basis representing an uncertainty of the net dipole on the order of 20–25%. In contrast, the dipole moments derived from 70 and 100 Ry calculations differ by only 0.01 a.u., for a relative uncertainty of 1–2%.

4. Discussion

CP correction does improve the GTF results towards the largest basis set results. We find that the CP-corrected BLYP binding energies for the T–A base pairs computed with the 6-31G(d, p) and 6-31 + + G(d, p) basis sets are very similar, −11.27 and −11.15 kcal mol^{-1}, respectively. However, with a significant increase in the number of large valence and diffuse functions, the aug-cc-pVTZ CP-corrected binding energy is predicted to be −10.87 kcal mol^{-1}. Since in the saturated basis limit we should achieve the exact BLYP binding energy, it should, in principle, be possible to extrapolate this value by determining the binding energy for a series of increasing larger basis sets. There are a number of works in the literature using basis extrapolation methods to determine the binding energy of small weakly bound systems such as the water dimer and trimer [7–11]. These methods appear to be most reliable when correlation consistent basis sets are used such as the aug-cc-pVxZ ($x = \mathrm{D, T, Q, 5, 6}$) series. Such methods are not practical for large systems because the basis set size grows rapidly within consistent hierarchies of basis sets.

Calculating the correct binding energy by the DFT-PW method is simply a matter of increasing the periodic cell dimensions and cutoff energy until the desired convergence is achieved. Better yet, it is now possible to modify the DFT-PW method such that electrostatic interactions between neighboring cells is eliminated [28] by truncating the electrostatic potential within a unit cell. This allows for the determination of the correct binding energy in a single set of calculations with modest cell dimensions. We are in the process of adding this feature to JEEP. Of course, truncation of the electrostatic interactions between periodic cells is not necessary when we wish to make predictions that are directly comparable to the wealth of single crystal DNA data that has been compiled over the last two decades [29].

Earlier GTF calculations on F–A base pairing found weak gas-phase interaction energies [30–33,21]. The most sophisticated calculations prior to this report, by Meyer and Sühnel [30], give MP2/6-31G(d, p)//HF/6-31G(d, p) CP-corrected binding energies for the F–A and T–A base pairs of −3.9 and −12.3 kcal mol^{-1}, respectively. This result suggests that the hydrogen bonding interaction of the F–A base pair is ∼3 times weaker than the T–A base pair. Meyer and Sühnel also find that at the B3LYP/6-31G(d, p) level, the F–A interaction is ∼4 times weaker than T–A. In our PW calculations, the ratio of T–A interaction energy to F–A interaction energy is larger (about 7:1), supporting Kool's argument that hydrogen bonding between F and A is negligible and that sterics play an important role in DNA replication fidelity [34]. Contrary to the conventional wisdom that electronegative atoms form strong hydrogen bonds (e.g., both the H_2O dimer and HF dimer have gas-phase binding energies of ∼5 kcal mol^{-1}), Howard et al. [35] report that fluorine bonded to a sp^2 carbon is a weak hydrogen bond acceptor. At the MP2/TZV + +(3d, 1f, 1p) level, the $CH_3F\cdots HOH$ and $CH_2{=}CHF\cdots HOH$ CP-corrected binding energies are only −2.38 and −1.48 kcal mol^{-1}, respectively. Interestingly, in our PW calculations, we find that the F–A electron density of the C–H···N hydrogen bond, which should be a weak interaction since C–H is a poor hydrogen donor, is about an order of magnitude higher than the F···H–N hydrogen bond, suggesting that the fluorine hydrogen bond is indeed very weak in the F–A base pair.

5. Conclusions

In this Letter we have determined the binding energy of three DNA base pairs using DFT with the BLYP exchange-correlation functional. We have demonstrated by using a plane-wave basis with periodic cells, a method inherently free of BSSE, that computed hydrogen bond energies, equilibrium geometries, and electrostatic multipole moments are virtually identical to the same properties obtained by expensive counterpoise corrected aug-cc-pVTZ calculations. This, of course, is not surprising as both methods should (and do appear to) converge in the

limit of complete basis set saturation and infinite cell dimensions and cutoff energies. Moreover, we have found that in comparison to our GTF calculations, the DFT-PW results are quite insensitive to the choice of cell dimensions and cutoff energies.

Acknowledgements

Calculations were carried out on the Lawrence Livermore National Laboratory Digital/Compaq Alpha clusters ''Compass'' and ''Tera'', and the Accelerated Strategic Computing Initiative Blue-Pacific IBM parallel computer. This work has been done under the auspices of the US Department of Energy, contract W-7405-ENG-48.

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