

A transferable electrostatic model for intermolecular interactions between polycyclic aromatic hydrocarbons

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Abstract

This work builds on our recently published anisotropic potential for polycyclic aromatic hydrocarbons (PAH) (*J. Chem. Theory Comput.* **2010**, 6, 683-695) by developing a new transferable electrostatic model for PAH molecules. Using this model, the atomic charge parameters used in the PAH anisotropic potential may be rapidly calculated from a set of predefined parameters rather than from molecule-specific *ab initio* calculations. The importance of the out-of-the-plane quadrupolar moments is highlighted and they are used as the basis for an accurate and transferable electrostatic model for PAHs. This model exhibits an r.m.s. deviation of 1.7 kJ mol^{-1} ; an order of magnitude less than previous models.

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1 Introduction

We have recently developed a transferable, anisotropic intermolecular interaction potential for pericondensed polyaromatic hydrocarbon molecules (PAHs) [36]. This potential, termed PAHAP, is based on accurate interaction energies calculated using the symmetry-adapted perturbation theory based on density functional theory (SAPT(DFT)) [19–21] and dispersion coefficients calculated using the Williams–Stone–Misquitta (WSM) method [17, 18, 22]. While the PAHAP potential has been developed to be transferable, it is not entirely so as molecule-specific ESP (electrostatic-potential-fitted) point charges are required to describe the electrostatic part of the interaction. The choice of ESP charges was made mainly for reasons of computational efficiency: they can be calculated using a number of quantum chemistry programs, and charge models are supported by practically every simulation program. There are other more detailed and accurate descriptions of the electrostatic interaction, the distributed multipole method [31, 32] being one of the most successful [4, 26]. However, despite the increased accuracy, proven in numerous numerical studies, these more complex models are largely unsupported by simulation programs. Consequently, in an attempt to balance accuracy, computational ease and usability, the PAHAP potential was developed to be paired with ESP charges. Therefore, it is these charges that form the reference against which all charge models will be compared with in this letter.

ESP charges are usually calculated from the overall molecular electrostatic potential obtained using an *ab initio* method, the most common of which is density functional theory (DFT). While this is not a problem for the smaller PAH molecules, the computational expense of the DFT calculations can be appreciable for the larger molecules, which can contain a few hundred atoms. Moreover, prototypical soot clusters are known to contain a large number of different PAH molecules that change dynamically in a flame environment [2, 5, 6, 27, 28, 30]. The calculation of *ab initio* point charge models for such a dynamically evolving cluster would be computationally expensive and is best avoided. Additionally, we encounter numerical instabilities from basis set linear dependencies which become severe for the larger PAH molecules. This makes it difficult to converge the DFT calculations without resorting to small basis sets, which in turn can result in a loss in accuracy.

One solution to this problem is to use the idea of *transferability*. The ‘honeycomb’ carbon structure common to pericondensed PAH molecules allows us to define a few common atomic site environments. The goal of a transferable electrostatic model is to model the charge distribution of all molecules based on the general description afforded by these transferable site types. If successful, such an approach would negate the requirement for computationally expensive *ab initio* calculations, as the charges would be computed for small molecules and *transferred* to large molecules.

This approach was taken in a recent paper by Herdmann and Miller [11]. In this model—which we will denote as ‘q/HM’—atom-centred charges were assigned based upon five different carbon site types (described below) and one hydrogen site type. The charges were taken from earlier work [12, 15] in which effective atomic charges were calculated using Hückel MO theory and Mulliken population analysis [24]. However, Mulliken charges are not necessarily the best charges to describe intermolecular electrostatic interactions [29].

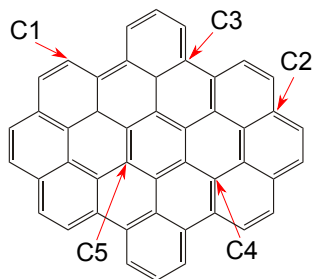


Figure 1: Definition of carbon site types in octabenzocoronene for the general set of point charges.

Furthermore, a serious limitation of the Herdman–Miller charge model is that no account is taken of the overall charge neutrality of the molecule. While for smaller molecules (in small clusters) a slight net charge will not manifest itself markedly in the calculated interaction energies, for larger molecules or large clusters a significant net charge can be present, leading to large repulsive electrostatic interactions. This precludes the direct use of such a charge model in a realistic simulation.

One way of getting around these limitations is to construct a general charge model based on ESP charges calculated for a range of PAH molecules, and to impose a charge neutrality condition. In this approach, the general charge, q_i , on each site type i can be defined as the average of the ESP charges of that site type in the molecules under consideration. We have done this for 13 PAH molecules (details are provided below and in the SI). Molecular charge neutrality can be imposed by using an alternative set of charges, q_i^* , derived from the original set, q_i , as follows:

$$\sum_i^N q_i^* = \sum_i^N \left(q_i - \frac{Q}{N} \right) = 0, \quad (1)$$

where $Q = \sum_i q_i$. We denote this charge model, the q_i^* , by ‘q/ESP’ (i.e., a ‘point charge model derived from ESP charges’).

The q/ESP model is a definite improvement over the q/HM model, with overall root mean square deviations in electrostatic energy (compared with the reference ESP models) of 6.1 kJ mol^{-1} versus 17.9 kJ mol^{-1} for the q/HM model, but it is still far from adequate. This can be clearly seen from the scatter plot of electrostatic energies for three PAH dimers shown in Figure 4. The dramatic charge neutrality violations of the q/HM model are corrected by the q/ESP model, and energies from this model follow the general trend of the reference ESP models, but the scatter of energies is far too large.

This should not be a surprise: with the exception of the terminal C–H groups, the atoms in a typical PAH molecule are largely uncharged and the relevant physical property (of the carbon atoms) is not the charge, but the *quadrupole moment*. Any model of transferability should therefore be based on quadrupole moments rather than effective charges. In this letter we describe such a physically motivated, transferable electrostatic model based on quadrupoles. Further, we demonstrate how such a model can be easily and efficiently transformed into an effective point charge model, which outperforms the standard transferable charge models described above by a substantial margin.

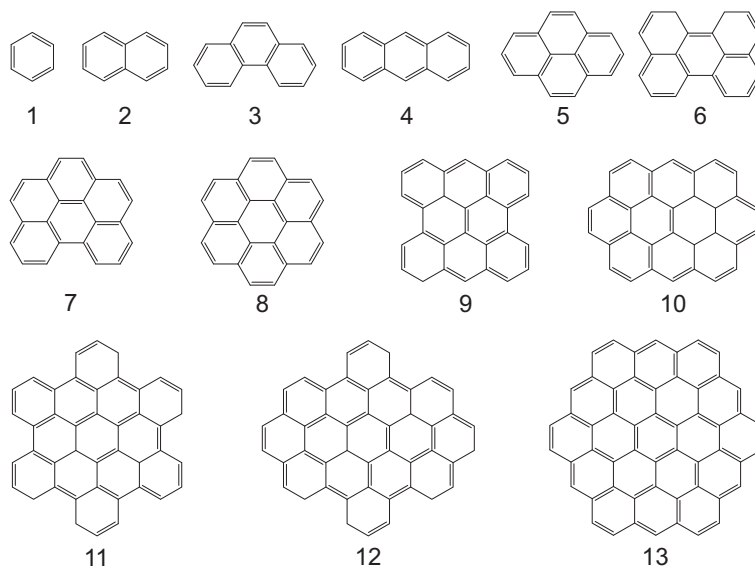


Figure 2: The pericondensed PAH molecules studied in this work: 1. Benzene (C_6H_6), 2. Naphthalene ($C_{10}H_8$), 3. Phenanthrene ($C_{14}H_{10}$), 4. Anthracene ($C_{14}H_{10}$), 5. Pyrene ($C_{16}H_{10}$), 6. Perylene ($C_{20}H_{12}$), 7. Benzo[*g,h,i*]perylene ($C_{22}H_{12}$), 8. Coronene ($C_{24}H_{12}$), 9. Bisanthene ($C_{28}H_{14}$), 10. Ovalene ($C_{32}H_{14}$), 11. Hexabenzocoronene ($C_{42}H_{18}$), 12. Octabenzocoronene ($C_{46}H_{18}$), 13. Circumcoronene ($C_{54}H_{18}$)

2 Methods

2.1 Atomic environments

The six atomic environments used by Herdman and Miller [11] have been used in this work to characterise the different positions of atoms within a PAH molecule. These are defined as follows: type C1, an edge carbon bonded to a hydrogen atom; type C2, an edge carbon bonded to two type C1 carbons; type C3, an edge carbon attached to a type C1 carbon and another type C3 carbon (*i.e.* a bay carbon); type C4 an interior carbon bonded to one or more edge carbons; type C5, a buried interior carbon bonded only to type C4 or type C5 carbons (see Figure 1). It should be noted that while symmetry considerations often reduce the number of different charge environments in a PAH molecule, these six site types are normally insufficient to match the actual number of different environments. However, these site types were found to provide enough fidelity to accurately reproduce the molecular potential, and they are unambiguously defined.

2.2 Reference charge models

Molecule-specific ESP point charge models for the 13 PAH molecules shown in Figure 2 were calculated using DFT with the PBE0 functional [1, 25] and the aug-cc-pVTZ [14] basis using the GAUSSIAN program [10]. Due to SCF convergence problems, for molecules larger than coronene the smaller cc-pVTZ basis was used. Table 1 shows the point charges

Table 1: ESP atomic point charges calculated for the coronene molecule. By symmetry, there are only three types of carbon atom for the coronene molecule: C1 corresponds to a carbon attached to a hydrogen, C2 corresponds to a carbon attached to two C1-type carbons and C4 corresponds to interior carbons attached to one C2-type carbon.

Method	C1	C2	C4	H
B3LYP/6-31G*	-0.20601	0.14894	-0.00817	0.13562
PBE0/cc-pVTZ	-0.23233	0.16482	-0.00812	0.15398
PBE0/aug-cc-pVTZ	-0.23977	0.18171	-0.01102	0.15443
q/HM ^a	-0.123	0.056	0.003	0.100

^a Herdman-Miller charges [11]

for coronene calculated with both the aug-cc-pVTZ and the cc-pVTZ basis sets. There are slight differences for the interior carbons (C2 and C4) when the diffuse basis functions used in the augmented basis set are excluded, but for the exterior carbon (C1) and hydrogen sites the results are very similar. Intermolecular interactions between PAH molecules tend to be dominated by the edge atomic sites, as in general, they are in closest contact with neighbouring molecules, therefore leading to stronger interactions. Thus, while using the un-augmented basis set for larger molecules is a compromise, it should not affect the results markedly.

For reasons stated in the Introduction, these charge models form the reference against which all other electrostatic models will be compared.

2.3 Method for comparison of models

We compare electrostatic models against the reference molecule-specific ESP charges using electrostatic energies calculated for 2500 quasi-random homomolecular dimer configurations for each PAH molecule. These conformations were generated from a Sobol sequence using the algorithm described in Ref. [23] and implemented in the CAMCASP program [16]. Evaluations of the electrostatic energy were performed using the ORIENT program [35]. R.m.s. deviations reported in this letter are calculated against these sets of 2500 electrostatic energies.

3 Model development

3.1 General ESP charges (q/ESP)

Using the reference molecule-specific ESP charges, a set of point charges were calculated for each molecule by averaging atomic charges according to the site types defined above. From these a general set of charges was calculated by averaging these modified molecule-specific values, weighted according to the number of site types in each molecule (Table 2).

As the benzene charges differ markedly from the charges of larger PAH molecules they were excluded from the average. The charge sets calculated for each molecule may be found in the Supporting Information. As explained in the Introduction, the final charge model is obtained using Eqn. (1) so as to ensure molecular charge neutrality. The resulting model is termed ‘q/ESP’.

Whilst for some molecules the q/ESP model was found to match the molecule-specific ESP charges adequately, for others the scatter of points was large and sometimes there was little improvement on the Herdman-Miller charges (q/HM) (Figure 4).

3.2 Molecule-specific multipole models

The problem with the above approach stems from the simple fact that PAH molecules do not exhibit strong charge separation (even at the edge C–H bonds, the charges involved are relatively small - around 0.1 a.u. on hydrogen and -0.1 a.u. on carbon), and the charge model is attempting to mimic the effect of the dominant quadrupoles from the carbon atoms. The precise way charges need to be assigned to the atomic sites to model these quadrupoles will depend on the PAH geometry. This geometry dependence introduces a non-transferable element in the charges, which manifests itself as a large scatter seen in Figure 4.

A more transferable and physical approach is to use higher ranking atom-centred multipole moments derived from the charge density directly. These can be determined directly from the molecular wavefunction using Stone’s distributed multipole analysis (DMA) [31, 34]. The GDMA program [33] was used to generate molecule-specific distributed multipole moments for each PAH molecule up to rank 4 (hexadecapoles) for the carbon atoms and rank 1 (dipoles) for the hydrogen atoms. These calculations were based on the same basis sets and wavefunctions we used to compute the reference ESP charges (section 2.2). Comparing the resulting multipole moments for each molecule, we found atoms could be described adequately in terms of the initial choice of six atomic environments, which arise naturally from the multipole description. In addition, it was found that the dominant carbon interaction was the quadrupole moment out of the plane of the molecule (Q_{20}) as previously noted by Hunter and Sanders [13], although the edge C–H units also contained charge and dipole terms which could not be ignored.

In the first instance a molecule-specific reduced multipole model was implemented which included only the charge, dipole and Q_{20} component of the quadrupole moment (term this model ‘DMA-Q20’). Other quadrupole and higher ranking moments were ignored. In order to develop an electrostatic-potential-fitted charge model from this model, which, following the notation introduced in the Introduction we will term ‘q/DMA-Q20’, we used a simple and rapid fitting algorithm [3, 7, 8, 37] which is implemented in the MULFIT program [9]. This algorithm analytically calculates the difference between the potential of the reference moments on each atom and the fitted charges on its neighbours, and therefore scales linearly with the number of sites. The algorithm is fast and can be implemented on the fly in calculations which model interactions of evolving molecules. Default MULFIT parameter values have been used for all calculations: 1.2 Å and 3 Å for the lower and upper shell bounds respectively, and 2 Å for the atomic radius.

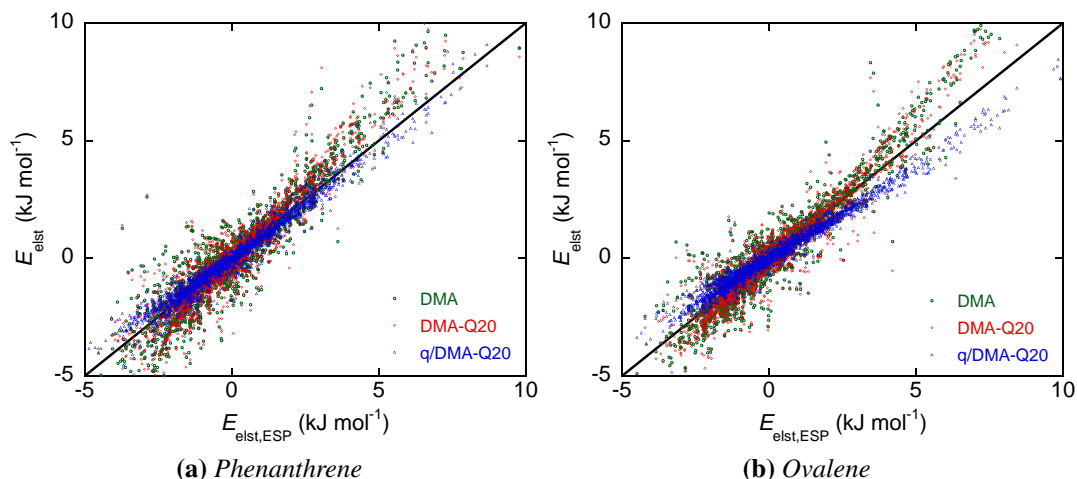


Figure 3: Comparison of electrostatic energies for 2500 random dimer conformations for representative PAH molecules, phenanthrene and ovalene, using different electrostatic models.

Interaction energies calculated using the resulting charge-only model (q/DMA-Q20) are compared with energies from the DMA and DMA-Q20 models against the reference energies from the molecule specific ESP charges in Figure 3. Here, representative PAH molecules have been chosen; phenanthrene ($C_{14}H_{10}$) and ovalene ($C_{32}H_{14}$), which between them possess atoms belonging to all six atomic environments.

The relative trends for each model are remarkably similar across all the PAH molecules, with the DMA-Q20 model behaving very similarly to the full DMA model. This indicates that the simplification of using only multipoles up to Q_{20} still captures the important characteristics of the overall molecular electrostatic potential. When comparing the models against the ESP charges the charge-only model calculated using MULFIT performs best with a reduced degree of scatter. This result is to be expected as both both ESP and q/DMA-Q20 are simple charge fits to the molecular electrostatic potential. When compared against higher order multipole models a scatter is seen, as the charge-only models are not able to model electrostatic interactions as accurately in certain conformations. All these models remain molecule-specific, but similar trends seen across the molecules, and the particularly good match seen using the q/DMA-Q20 charges, suggest that a transferable electrostatic model is achievable.

3.3 A transferable multipole model (qQ20)

The DMA-Q20 model is accurate but can be further simplified without a significant loss in accuracy. For interior carbons the Q_{20} quadrupole moment dominates, as both charge and dipole terms are small and, as has already been mentioned above, the effect of the higher order terms is negligible. This leads to the first simplification in which we discard the charge and dipole terms on the interior carbon atoms. A further simplification can be achieved by replacing the dipole moments on the edge C–H atoms by effective charges.

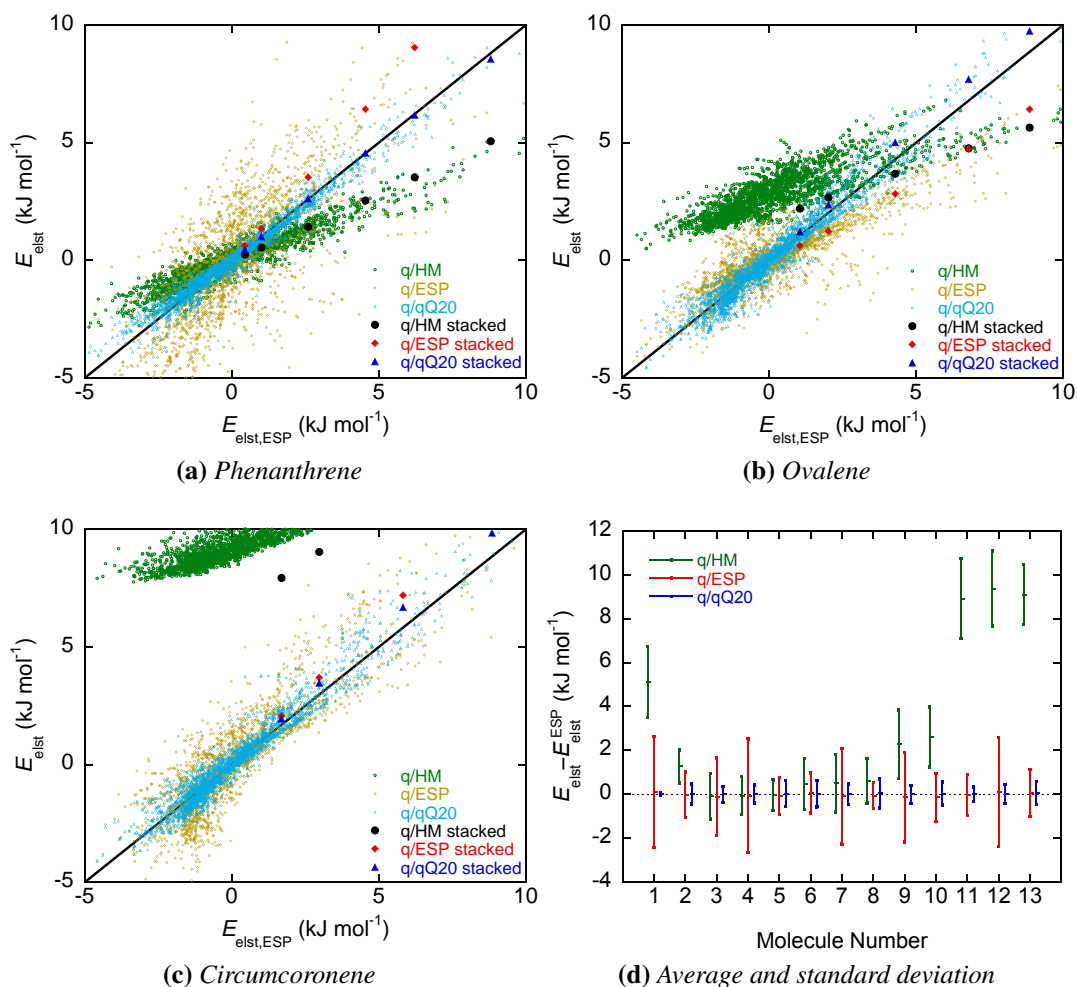


Figure 4: Comparison of electrostatic energies calculated using three general electrostatic models: Herdman-Miller charges (q/HM), general ESP charges (q/ESP), general multipole model based on carbon Q_{20} moments and periphery charges (q/q Q_{20}). Energies have been calculated for 2500 random phenanthrene, ovalene and circumcoronene dimers. Sub-figure (d) contains average deviations of the electrostatic models from the reference ESP charge models (the centre of the sticks) together with the standard deviations of these differences (the stick half-length). The molecule number refers to the molecules shown in Figure 2.

This resulting model which we describe below is what we call the ‘q Q_{20} ’ model, that is, it includes charges and Q_{20} moments only.

We obtained a general set of Q_{20} moments using the approach adopted for the q/ESP model (section 3.1). For each molecule Q_{20} moments were averaged according to the five carbon types (details provided in the Supporting Information). Subsequently a general set of transferable Q_{20} moments were calculated by averaging over all molecules. The resulting Q_{20} moments for each site type together with their standard deviations are shown in Table 2. The small standard deviations seen in the averaged set of moments supports the choice of five carbon types, and indicates that the Q_{20} moments are far more transferable

Table 2: Summary of parameters for q/ESP and $qQ20$ electrostatic models. The standard deviations for the q/ESP charges and Q_{20} moments, calculated when averaging across all PAH molecules, are given in brackets.

Model	Moment	H	C1	C2	C3	C4	C5
q/ESP^a	q	0.152 (0.015)	-0.231 (0.091)	0.225 (0.034)	0.047 (0.022)	-0.011 (0.026)	-0.010 (0.023)
$q/qQ20^b$	q	-0.01746	0.01746				
	Q_{20}		-1.280 (0.014)	-1.114 (0.001)	-1.134 (0.002)	-1.158 (0.002)	-1.161 (0.002)

^a Charges are used with the charge neutrality criterion (Eqn. 1).

^b Charges and Q_{20} moments are combined to give charge-only models using MULFIT [9].

than the charges in the q/ESP model.

The charge and dipole moments cannot be ignored for the edge C–H groups. In principle these terms can be retained, though this would require a local axis frame on all edge sites to orient the dipole moments appropriately. In practice, a simpler solution is to fit some of the dipole moment character into effective charge terms on the edge carbon and hydrogen atoms. If the charges chosen are constrained to be equal and opposite, then charge neutrality is ensured. There is some degree of arbitrariness about the choice of charges, but we have found that the best results (when compared with our ESP references) are obtained using edge charges derived using the benzene molecule. We obtained edge charges by transforming the dipole moments on the atoms of benzene into effective charges using the MULFIT program to obtain *total* effective charges of +0.01746 a.u. on the carbon atom and -0.01746 a.u. on the hydrogen atom. We note that the symmetry of benzene naturally results in charge neutral C–H groups. These charges are an order of magnitude smaller than the equivalent ESP charges and are contrary in sign to what would be expected on the basis of the electronegativity of carbon and hydrogen. These charges, together with the Q_{20} parameters complete the $qQ20$ transferable electrostatic model for PAH molecules. A summary of the parameters for $qQ20$ model is given in Table 2.

3.4 Transforming the $qQ20$ model into effective charges ($q/qQ20$)

The $qQ20$ model allows us to construct an accurate charge and quadrupole electrostatic model for any (planar) PAH molecule, from which we can derive an effective charge model using the MULFIT program. The steps involved are:

1. Place the PAH molecule in the xy -plane. This is to ensure that the Q_{20} moments are along the z -axis.
2. Assign charges to the edge C–H sites.
3. Assign the appropriate Q_{20} quadrupole moments to the carbon atoms.

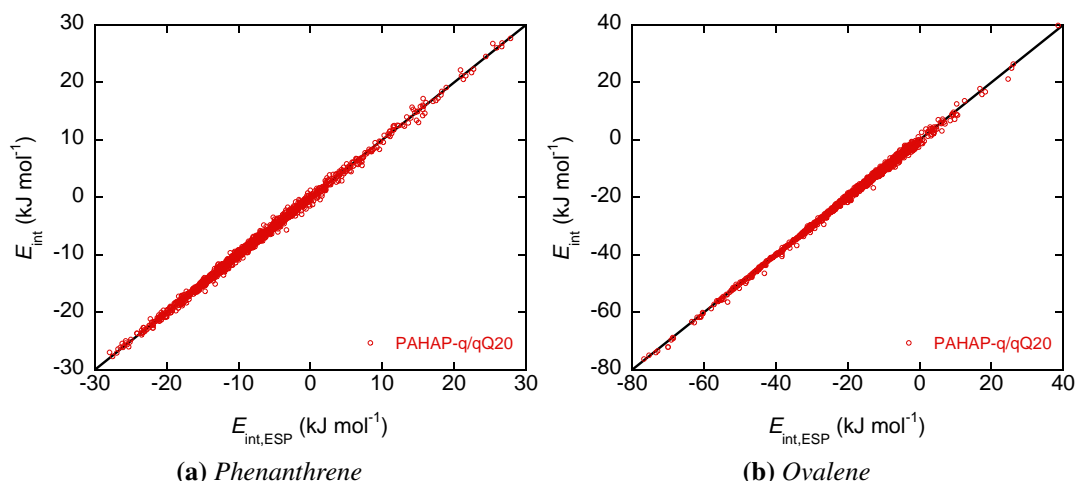


Figure 5: Comparison of PAHAP interaction energies using new *q/qQ20* electrostatic model against normal PAHAP energies using ESP charges for 2500 phenanthrene and ovalene dimer conformations.

4. Use the MULFIT program to transform this charge-quadrupole model into an effective charge-only model.

The final molecule-specific effective charge model will be termed ‘*q/qQ20*’, that is, a charge model derived from the transferable *qQ20* multipole model.

Figure 4 compares the energies calculated with the Herdman-Miller charges (*q/HM*), the general ESP charges (*q/ESP*) and the *q/qQ20* charges against the reference energies from the specific ESP charges for representative PAHs. The *q/qQ20* models are clear improvements over the *q/HM* and *q/ESP* models with an overall root mean square deviation from the reference charges over all energies calculated for all 13 PAH molecules of only 1.7 kJ mol^{-1} . This compares with 6.1 kJ mol^{-1} for the *q/ESP* model and 17.9 kJ mol^{-1} for the *q/HM* charges. Additionally, the overall trends of the *q/qQ20* models are far better, particularly at the stacked conformations which tend to represent minimum energy conformations. Furthermore, charge-neutrality is imposed naturally in the *q/qQ20* models. This contrasts with the somewhat arbitrary neutrality condition imposed on the *q/ESP* model which introduces an increased scatter, and the complete absence of neutrality in the *q/HM* model which results in increasingly over-repulsive and unphysical energies, particularly for the larger PAH molecules. Overall, the *q/qQ20* models derived from the transferable *qQ20* charge and quadrupole model represents a significant improvement over any existing transferable charge model for PAH molecules.

In the overall interaction potential the dispersion and exchange-repulsion terms tend to make up the bulk of total interaction and hence as a proportion of the total energy of the interaction an error of $1\text{--}2 \text{ kJ mol}^{-1}$ is acceptable (Figure 5).

4 Conclusions

In conclusion, we have obtained a transferable set of parameters which accurately describe the electrostatic interactions of PAH molecules in terms of atom-centred charges and quadrupole Q_{20} moments. This qQ20 model can be easily and efficiently transformed into an effective charge model, q/qQ20, using the MULFIT program. The resulting q/qQ20 effective charge models accurately reproduce electrostatic interactions for PAH dimers with an r.m.s. deviation of 1.70 kJ mol^{-1} from reference energies calculated from *ab initio* ESP charges for 13 PAH molecules. This compares favourably with the r.m.s. deviation of 6.13 kJ mol^{-1} for the q/ESP charges derived from a set of general ESP charges using a simple charge neutrality condition, and 17.9 kJ mol^{-1} for the Herdman-Miller charges taken from Ref. [11]. The q/qQ20 models are also shown to reproduce electrostatic energies in stacked PAH conformations very accurately which is important as these tend to represent the minimum energy conformations.

The improvement we observe is due to a better physical description of the charge distribution around PAH molecules using the quadrupole Q_{20} moments which dominate the electrostatic interaction. The Q_{20} moments found for each of the defined atomic environments remain essentially constant across all PAH molecules, demonstrating their transferability. This is not the case for averaged ESP point charges which necessarily include some molecule-specific geometry dependence. In addition to the Q_{20} moments small charges are placed on edge C–H atoms to account for charge and dipole character of these atoms. By choosing these charges to be equal and opposite, molecular charge neutrality is ensured in the transformed molecule-specific charge models.

Our main motivations for developing a transferable electrostatic model for PAH molecules were (1) to avoid the need for computationally expensive *ab initio* calculations during a simulation, (2) that the model be physically motivated and (3) to be able to calculate the electrostatic interaction between PAH molecules to an accuracy comparable to that of the PAHAP potential to which this model is paired. The qQ20 model satisfies all of these conditions. Additionally because of its physical grounding, this model is general enough to be used on systems other than planar PAH molecules; for example, PAH molecules with side groups, non-planar PAH molecules, and possibly even fullerenes.

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