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Journal of Chemical Theory and Computation

Dispersion Corrected Atom-Centered Potentials for Phosphorus

Michele Cascella,[†] I-Chun Lin,[‡] Ivano Tavernelli,[§] and Ursula Rothlisberger^{*,§}

Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland, Department of Chemistry, New York University, 100 Washington Square East, Room 1001, New York, New York 10003-6688, and Laboratory of Computational Chemistry and Biochemistry, Institute of Chemical Sciences and Engineering, BCH 4109 Ecole Polytechnique Fédérale de Lausanne EPFL, CH-1015 Lausanne, Switzerland

Received July 20, 2009

Abstract: Dispersion-corrected atom-centered potentials (DCACPs) for the element phosphorus were generated and tested for the BLYP, BP, and PBE generalized gradient approximations of the exchange–correlation functional. The accuracy and transferability of the DCACPs were tested by evaluating the interaction energy of different weakly bound molecular systems (P₂, PH₃, and PN dimers). These results were compared to reference CCSD(T) calculations and standard density functional theory (DFT). The DCACP were also tested in the case of condensed phase systems. Specifically, the density and cohesive energies of β -white and black phosphorus were estimated and compared to available experimental data. Our results show an overall strong improvement both at the qualitative and quantitative level, with respect to uncorrected generalized gradient approximation DFT results for all three functionals. In particular, BLYP-corrected results show the maximal transferability, reporting for all systems a deviation from CCSD(T) results of less than 1% in the predicted binding energies.

Dispersion forces are a crucial type of interaction that influence many chemical and physical phenomena. At the same time, these forces are very difficult to capture by first

principles calculations, due to the fact that they originate from dynamical correlation of the electronic degrees of freedom. In particular, density functional theory (DFT) with standard approximations of the exchange–correlation (xc) functional is quite weak in describing dispersion interactions.^{1–4} Recently, different possible corrections to DFT that include dispersion interactions have been proposed. Different schemes presented in the literature make use of electron density partitioning,⁵ solution of the adiabatic connection formula for the long-range part of the interaction energy,⁶ symmetry adapted perturbation theory,^{7,8} sophisticated approximation of the xc-potential,^{9,10} or add an explicit “dispersion interaction” term with a C₆ coefficient either determined empirically^{3,11,12} or generated by the instantaneous dipole moment of the exchange hole.^{13–15} Very good results have also been achieved by Truhlar and co-workers with hybrid meta-generalized gradient approximations (GGA) of the xc functional.^{4,16,17} It has been shown that dispersion interactions can also be empirically included as correction to the total Kohn–Sham potential, expressed in the form of a multicenter density functional.^{18–23} In our scheme, the atom-centered corrections are determined via a penalty function that minimizes the DFT data with respect to a reference calculation at high-level (typically, CCSD(T)). These dispersion-corrected atom-centered potentials (DCACP) have been shown to be highly transferable and to provide good results in reproducing binding energies in different systems, like inert gases,²⁴ aliphatic and aromatic hydrocarbons,²⁵ stacked base pairs,²⁶ and hydrogen-bonded complexes.^{27,28} DCACPs have been developed for local forms of the approximate xc functionals (typically, GGAs), which ensure the broadest applicability in both Gaussian and plain-wave based codes. Currently, DCACPs are available for inert gases and for hydrogen, carbon, oxygen, nitrogen, and sulfur elements.^{24,29} In this letter, we present the results for phosphorus, thus, completing the library of the main elementary constituents of biological matter.

The theory and methodology to develop DCACPs have been widely discussed elsewhere.^{18,24} Briefly, the electronic problem is solved in the presence of an atom-centered correction potential:

$$H = H_0 + \sum_i V_{ik}(R_i - r) \quad (1)$$

where H_0 is the standard Kohn–Sham Hamiltonian, and V_{ik} is the correction potential, centered on each atom i , specific for each element k . Each V_{ik} has the form of a Gaussian and is tuned through a penalty function to reproduce dispersion

* Corresponding author. Telephone: +41-(0)21-6930321. Fax: +41-(0)21-6930320. Email: ursula.roethlisberger@epfl.ch.

[†] Universität Bern.

[‡] New York University.

[§] Ecole Polytechnique Fédérale de Lausanne EPFL.

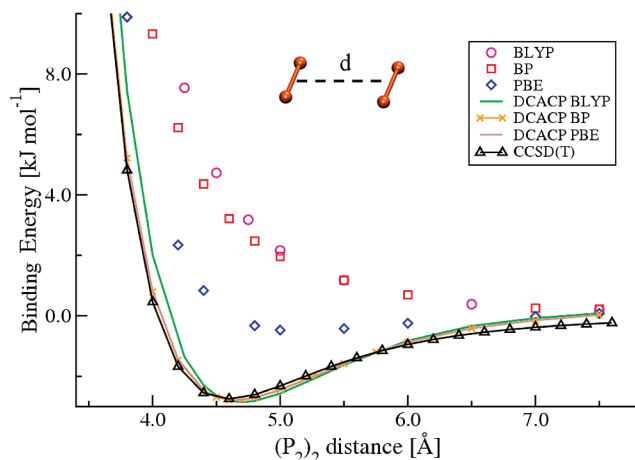


Figure 1. Calibration of DCACP for the phosphorus element based on P_2 dimer interactions. Results for BLYP, BP, and PBE xc functionals are shown with respect to the CCSD(T) reference plot.

dominated reference interaction energies, calculated for a simple system by a high-level methodology (CCSD(T)). DCACPs are, by design, effective corrections to a given approximate form of the xc functional.³⁰ Therefore, different DCACPs have to be generated and used for calculations using different xc functionals.

In our case, reference dispersion interactions in phosphorus were evaluated for the $(P_2)_2$ system. First, we optimized the geometry of the P_2 molecule at MP2/aug-cc-pVTZ level, finding a P–P distance of 1.927 Å. Then, we calculated the interaction energy for the $(P_2)_2$ moiety as a function of the distance of the two relative centers of mass, constraining the two P_2 molecules in a parallel D_{2h} conformation (Figure 1). The electronic problem was solved at the CCSD(T)/aug-cc-pVTZ level of theory, taking into account standard counterpoise corrections. Geometry optimization and interaction energy calculations were performed using the GAUSSIAN03 package.³¹ DFT calculations were performed using the CPMD code,³² simulating the system in an isolated box of $23 \times 15 \times 15 \text{ Å}^3$, using plane-waves with a cutoff of 200 Ry as basis functions and employing the pseudopotential of Goedecker et al.³³ Details on the calibration procedure can be found in refs 18 and 24. The parameter sets for the obtained DCACPs can be downloaded at <http://lbcpc21.epfl.ch> (see also Supporting Information).

The interaction energy plot obtained by CCSD(T) calculations shows a minimum energy of about 2.65 kJ mol^{-1} for an intermolecular distance of 4.6 Å (Figure 1). As expected, DFT based on GGAs of the xc functional poorly describe this interaction. In particular, Becke–Lee–Yang–Parr (BLYP)^{34,35} or Becke Perdew (BP)³⁶ xc functionals show a completely repulsive profile.

Perdew–Burke–Ernzerhof (PBE)³⁷ GGA results in a very shallow minimum at an intermolecular distance of about 5 Å. On the other hand, including DCACPs leads to good agreement of the DFT energy plots with the CCSD(T) reference curve for all three xc functionals taken under consideration (Figure 1). The largest deviations are found for the results with the corrected BLYP functional, which show an equilibrium distance of about 4.75 Å, approximately 0.15 Å longer than the CCSD(T) result. The faster decay of the long-range tail in the DCACP plots is related to the fact that DCACPs are represented with a single

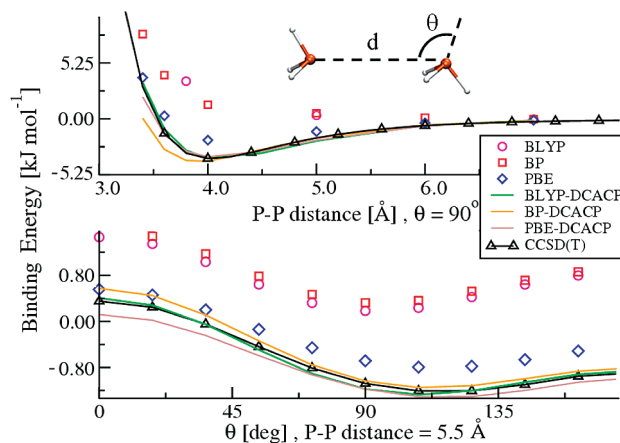


Figure 2. Top panel: interaction potential of two phosphine molecules as a function of the P–P distance. Bottom panel: interaction potential at fixed distance ($d = 5.5 \text{ Å}$) as a function of the relative orientation.

(nonlocal) angular momentum channel (f) that leads to minimal errors in the energy of the minimum, but it is not sufficient to completely ensure a formally correct long-range behavior.³⁰ The use of a single channel constitutes the best compromise between accuracy and computational cost for the DCACP method.

The transferability of the newly obtained DCACPs was tested on a set of systems where dispersion interactions contribute substantially to the energetics. The first system we used is the phosphine dimer $(PH_3)_2$. The geometry of a single phosphine molecule was first optimized at the MP2/aug-cc-pVTZ level. Then, two phosphine molecules were oriented at a relative angle $\theta = 90^\circ$ (where θ is the angle between the two principal symmetry axes of the PH_3 molecules, see Figure 2) to nullify the dipolar interactions. In this case, as in all heterogeneous compounds, DCACPs calculations were performed using DCACP-corrected potentials for both phosphorus and hydrogen elements. Additivity, transferability, and comparability of DCACPs for heterogeneous systems have been broadly discussed and successfully tested in previous papers^{24–30} (see also Supporting Information). The binding energy as a function of the phosphorus–phosphorus distance was then evaluated. Figure 2 (top panel) reports the results obtained for GGA and DCACP calculations. DCACPs substantially improve the DFT/GGA results, leading, in the case of BLYP and PBE, to binding energies and equilibrium distances equal to those obtained by CCSD(T) calculations. The BP corrected functional, on the contrary, shows a slightly softer curve.

The bottom panel of Figure 2 shows the interaction potential of the two phosphines at a P–P distance of 5.5 Å when rotating the angle θ . Also in this case, the overall quantitative agreement of the DCACP results, with respect to the CCSD(T) reference, is very good. In particular, the location of the minimum at $\sim 115^\circ$ and the relative energies of the local and global maxima at 180° and 0° , respectively, are all features that are quantitatively not well reproduced at the uncorrected DFT level. The DCACPs for phosphorus account for more than 95% of the correction to the binding energy.

A second test for the transferability of P-DCACPs was performed on the unusual PN molecule. Due to the peculiar electronic nature of this molecule, this system can be considered as a challenging test for the transferability properties of

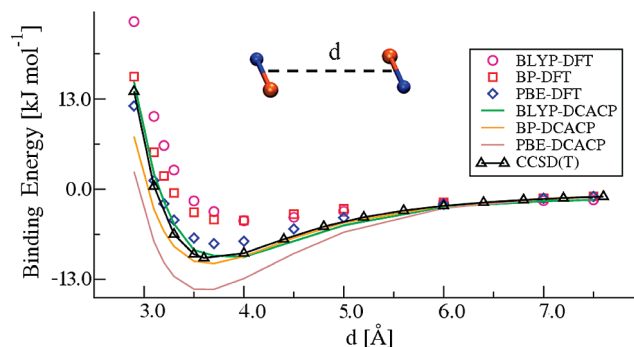


Figure 3. Interaction potential of two PN molecules placed in planar C_{2h} configuration (molecules perpendicular to d axis).

DCACPs. Figure 3 reports the results for this system in C_{2h} symmetry (molecules oriented perpendicular to the axis passing through their respective geometrical centers). In this case, the xc functionals based on the Becke exchange report a shallow minimum at about 3.8 (BP) and 4.0 Å (BLYP). This points to the fact that the $(PN)_2$ moiety is not bound by pure dispersion forces, but there is an additional stronger interaction present between the two PN molecules (e.g., attractive dipole–dipole interactions due to bond polarity).

However, also in this case both BP and BLYP underestimate the binding energy, with respect to CCSD(T) results (4.47 kJ mol^{−1} instead of 9.71 kJ mol^{−1}). CCSD(T) calculations also predict a shorter equilibrium binding distance of 3.64 Å.

Dispersion-corrected BLYP and BP are again able to well reproduce the CCSD(T) data. PBE GGA is already fairly close to the CCSD(T) results, providing a binding energy of 7.88 kJ mol^{−1} and a bond length of 3.72 Å. In this case, the DCACP correction to PBE xc improves the binding distance to match the CCSD(T) result but leads to an overestimation of the $(PN)_2$ binding energy (~ 15 kJ mol^{−1}). DCACP data were obtained combining the corrected potential for P with the one of N.²⁴ Also in this case, the use of DCACPs on P only accounts for most of the binding energy correction. In Table 1, binding energies and distances of the three molecular systems are compared with the corresponding data obtained with the M06–2X xc functional.⁴ DCACP binding energies are closer to the CCSD(T) data than those predicted by M06–2X, while DCACPs and M06–2X perform comparably in predicting binding distances with respect to the CCSD(T) reference calculations.

A final transferability test was done by estimating the density of crystalline β -white phosphorus. Its primitive cell contains

Table 1. Binding Energies and Equilibrium Distances for P_2 , PH_3 , and PN dimers from Both Uncorrected and DCACP-Corrected DFT/GGA Results^a

molecule	BP	PBE	BLYP	DCACP BP	DCACP PBE	DCACP BLYP	M06-X2	CCSD(T)
$(P_2)_2$								
binding energy ^b	>0	−0.56	>0	−2.65	−2.65	−2.65	−1.83	−2.65
equilibrium distance ^c	—	5.00	—	4.60	4.60	4.75	4.50	4.60
$(PH_3)_2$								
binding energy ^b	>0	−1.64	>0	−3.19	−3.16	−3.17	−3.51	−3.17
equilibrium distance ^c	—	4.20	—	3.85	4.0	4.0	3.9	4.0
$(PN)_2$								
binding energy ^b	−4.47	−7.88	−4.47	−9.94	−14.81	−9.70	−14.01	−9.71
equilibrium distance ^c	3.85	3.70	4.0	3.68	3.63	3.74	3.50	3.64

^a The table presents a direct comparison with other xc approximation (M06–2X)⁴ and high-level CCSD(T) results. ^b Binding energies (kJ mol^{−1}). ^c Equilibrium distances (Å).

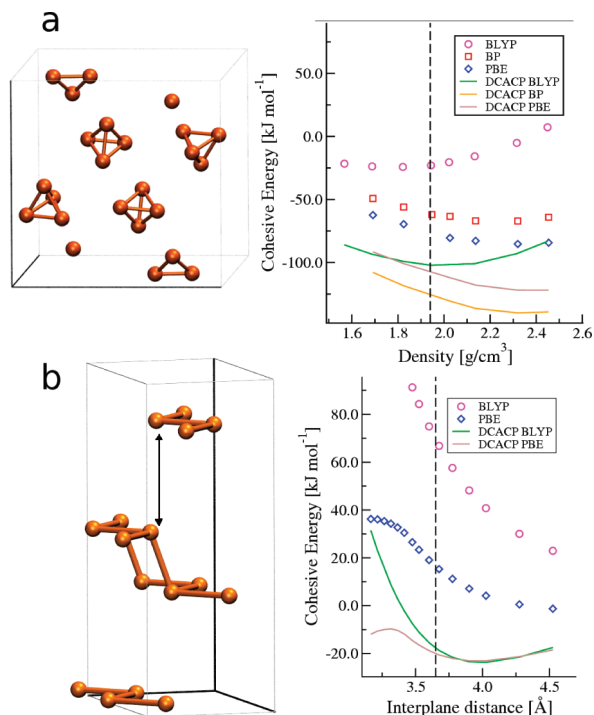


Figure 4. (a) Left panel: primitive cell of β -white phosphorus. Right panel: cohesive energy as a function of its density for different GGA and DCACP-corrected functionals. (b) Left panel: primitive cell of black phosphorus. Right panel: cohesive energy as a function of the P–P interplane distance (black arrow, left panel). The dashed lines in the two graphs indicate the corresponding experimental values.

six P_4 molecules, placed in symmetric pairs with respect to the center of the unit cell (Figure 4a, left panel).³⁸ This allotropic form of phosphorus is formally a molecular crystal, and therefore, the cohesive forces are expected to have strong dispersion contributions. However, the minimal distance among P atoms of different P_4 units can be as short as 3.1 Å, well below the typical van der Waals (vdW) distance of phosphorus; therefore, covalent terms also contribute to the cohesive energy.

In our calculations, we performed isotropic variations of the periodic cell. This means that the angles α , β , γ , and the relative ratio between the edges of the cell (a , b , c) were left unchanged with respect to the experimental values. Figure 4 reports the cohesive energy per P_4 molecule (calculated as: $E_c = E(\text{crystal})/6 - E(P_4)_{(\text{in vacuo})}$), as a function of the density of the crystal. Standard BLYP calculations predict the crystal to be only marginally stable at densities that are too low, with respect to

the experimental one (1.92 g/cm^3).³⁸ In fact, the BLYP xc predicts a density of $\sim 1.82 \text{ g/cm}^3$, which is, incidentally, the experimental density of the more expanded α -white phosphorus. On the contrary, BLYP-DCACP is again in excellent agreement with experiment, predicting a density of 1.92 g/cm^3 , identical to the experimental value. Both uncorrected BP and PBE functionals overbind the P_4 molecules, predicting a density of more than 2.0 g/cm^3 . Addition of the DCACP correction does not lead to an improvement of the results but only yields a constant energy shift. In fact, DCACPs cannot correct intrinsic DFT errors to binding energies for systems where the uncorrected xc functionals produce spurious covalent features. In order to confirm the differences in the intrinsic performance of the different xc functionals for covalent interactions, we have performed a final test on the structure of black phosphorus, a more compact allotropic form, where atoms bind covalently in layers displayed parallel to the x - y -plane, which then pack along the z -direction (Figure 4b). We have progressively varied the distance among layers (that is, varying the length of the edge along z of the periodic cell), forcing the single layer to remain in the same geometry along the x - y -directions and calculating the cohesive energy for every step. In this case, both BLYP and PBE functionals predict a repulsive behavior in the vdW distance region. DCACP-corrected functionals report the same energetics in the vdW region, with a minimum at around 3.8 \AA (Figure 4b). At closer distances, on the contrary, the PBE functional predicts a maximum around a distance of 3.2 \AA , followed by a reactive profile, which leads to covalent binding of the layers. As in the previous case, the behavior at covalent distances cannot be corrected by DCACP.

In summary, we present DCACPs for the phosphorus element in combination with BLYP, BP, and PBE xc functionals. Our benchmark calculations show that these potentials have a good transferability in systems dominated by dispersion interactions, as previously found for rare gases and second-row elements, already discussed in the literature. Tests performed on the unusual molecule PN, as well as on different allotropic forms of solid P, show that DCACP correction for BLYP keeps its good transferability in systems where the binding energy has dispersion and covalent components, while results from corrections to PBE may not be as accurate in such cases. Overall, the DCACP correction coupled to the BLYP functional performs best, as already reported for other elements (see refs 24–29). This work completes the DCACP library for “biological” elements, after the DCACP development for H, C, N, O,²⁴ and S²⁹ and, therefore, is of particular interest for studies of biochemical events involving phosphorus chemistry. Due to the sizable dispersion contributions of the phosphorus atoms, the DCACPs presented here are expected to be crucial for studies of nucleic acids, protein cofactors (FMN, FAD, NAD, etc...), enzyme-phosphorylated substrate complexes (e.g., in active sites of kinases), or in studies of protein transition-state analogue-based inhibitors.³⁹

Acknowledgment. The presented work was funded by the Swiss National Science Foundation (grant N. 200020-116294). The authors thank Dr. Mauricio D. Coutinho-Neto for useful discussion.

Supporting Information Available: DCACP potentials for the phosphorus element in Goedecker–Teter–Hutter format and comparison of DCACP parameters for different elements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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CT9003756