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A. V. LARIN,[1,2] **V. S. PARBUZIN,**[2] **D. GP. VERCAUTEREN**[1]

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ABSTRACT: Atomic multipole moments (AMMs) for aluminophosphate sieves (ALPOs) were evaluated considering the electron density (ED) computed with the CRYSTAL98 code at various periodic Density Functional Theory (PDFT) levels as well as basis sets. Using the EDs calculated with B3LYP, Perdew-Wang (PW91), and Perdew-Burke-Ernzerhof (PBE) functionals, "Mulliken" AMMs were computed within the scheme developed by Saunders et al. and approximated using a cumulative coordinate (CC) scheme similar to the one developed earlier for AMMs calculated from Hartree-Fock EDs. The convergence of the AMMs with the basis set is discussed. © 2004 Wiley Periodicals, Inc. Int J Quantum Chem 100: 000–000, 2004

Key words: periodic DFT; atomic multipole moments; aluminophosphate sieve

Introduction

The development of hybrid quantum mechanics / molecular mechanics (QM/MM) methods to tackle chemical reactivity is continuously expanding over new classes of chemicals. Several problems, however, remain unsolved regarding the QM/MM application to microporous and mesoporous crystals containing channels or cavities of large sizes, which hence can act as catalysts or supports for a catalyst in which co-adsorption and chemical reactions of large organic molecules become possible. For such materials, the direct solution of Schrödinger's equation is indeed usually not feasible as a result of the large lattice dimensions and huge number of atomic orbitals to consider. Hence, the construction of the MM part around the

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"small" embedded cluster is generally based either on an empirical periodic scheme whose parameters are optimized using ab initio calculations for large clusters similar to the crystalline material [1], or on the consideration of more expanded crystalline fragments treated at a lower theory level [2]. If these methods have been proven successful for several classes of materials, they unfortunately do not look relevant for materials such as aluminophosphate (ALPO) sieves, whose ionic nature results in important electrostatic energy gradients which are important for the crystalline stability as well as for the stabilization of adsorbed particles. The isolated cluster method often used for aluminosilicates could hence not be applied to these materials [3]. The QM/MM approaches should therefore be clearly completed with accurate estimations of the electrostatic part such as proposed with the cumulative coordinate (CC) technique [4]. As shown earlier, the CC technique allows one to define "interatomic" relations for the high-order Mulliken atomic multipole moments (AMMs) of each crystallographic type of atom in 3D solids [4] on the basis of Stone's equation [5]. Its principal advantage is that it does not deal with the AMMs themselves but with their dependences relative to the atomic geometries and lower-order AMMs of the neighbor atoms starting from the lowest AMMs, i.e., the atomic charges. And interestingly, it has also been shown that the latter can be obtained from analogous ab initio dependences of the charges with respect to their geometrical parameters [6–9] at a high level of theory for "small size" systems and hence provide accurate charge values for any arbitrary structure if its geometry is known [6]. While the AMMs depend on the local geometry (bond lengths, bond angles) of each atom which varies between the sites, as shown in the literature [10, 11], their CC dependences within a given computational method and basis set do not vary [4].

Our opinion is that future techniques which could be applied within QM/MM approaches should be universal enough with respect to the method used for electron density (ED) computation. Hence, we asked ourselves if the CC scheme already proposed for aluminosilicates and ALPOs [4] could be adopted using EDs calculated by Density Functional Theory (DFT) methods with the same precision as the AMMs obtained from periodic Hartree-Fock (PHF) [4]. And, moreover, would there be convergence of the atomic charges and/or AMMs while improving the basis set in materials such as ALPOs similarly to the Mulliken charges in all-siliceous systems [5, 12]? To answer these questions, we thus extended a similar type of analyses in terms of the CC technique for the ED and AMMs calculated by PDFT methods.

In the next section we present the theory, mainly summarizing Ref. 4, followed by explanations on the computational aspects as well as on the models of the considered ALPOs. Then we discuss the CC approximations obtained at different theory and basis sets levels, together with comparisons with available experimental data.

Theory of the AMMs Approximation

Both distributed multipole analysis methods used herein were developed [5, 13] as a continuation of the Mulliken partition scheme of the electron density (ED). As explained in Ref. 4, Stone's expression (Eq. 1) allows one to develop simple analytical approximations for the atomic multipole moments (AMMs) of a given crystallographic independent atom $Q_L^m(A)$ (L and m being the order and component of the AMM, respectively) with respect to the charge and geometry of respective fragments, including its N neighbors [5], even if only the very first term of Eq. 1 is considered:

$$Q_L^m(A) = \sum_{i=1}^{N}\sum_{S=0}^{L}\sum_{P=-S}^{S} a_{LmSP}\, Q_S^P(i)\, R_{L-S}^{m-P}(A, i)$$

$$= \sum_{i=1}^{N} a_{Lm00}\, Q_0^0(i)\, R_L^m(A, i) + \cdots . \quad (1)$$

where $a_{LmSP} = \left[\binom{L+m}{S+P}\binom{L-m}{S-P}\right]^{1/2}$, i running over all nearest neighbors in the first shell of atom A, $Q_0^0(i)$ is the Mulliken charge of the i neighbor, and $R_L^m(A, i)$ corresponds to the Legendre polynomial whose argument is the vector between the considered atom A and site i [5]. Then, one can deduce the coordinates for the charge and geometry dependences of the AMMs from Eq. 1 as:

$$Q_L^m(A) = a_{Lm00} R_L^m(A) + b_{Lm00} \quad (2)$$

where a_{Lm00} and b_{Lm00} are fitting parameters, and $R_L^m(A)$ functions correspond to the unnormalized functions $X_L^m(A,i)$ as considered in CRYSTAL [14]:

TABLE I

Symbols, number of atoms per unit cell (UC), of different Al, P ($n_P = n_{Al}$), and O types, of atomic orbitals (AO) per UC, and symmetry group of the aluminophosphate (ALPOs) sieves,[a] all of them corresponding to the Al/P = 1.

Name	Symbol	Atoms/UC	n_{Al}/n_O	AO/UC (6-21G** (BS3))	Symmetry group
AlPO$_4$-41	AFO	60	4/13	920	Cmc2$_1$
AlPO$_4$-18	AEI	72	3/12	1,040	C2/c
AlPO$_4$-5	AFI	72	1/4	1,104	P6cc
AlPO$_4$-H2	AHT	36	2/7	552	Cmc2$_1$
AlPO$_4$-31	ATO	36	1/4	552	R3
MeAPO-39	ATN	24	1/4	432	I4
Berlinite[b]	—	18	1/4	276	P3$_1$21

[a] Coordinates from Ref. 16.

[b] Coordinates from Ref. 17.

$$R_L^m(A) = \sum_{i=1}^{N} Q_0^0(i)\, X_L^m(A, i) \qquad (3)$$

instead of the *R*Lm function (used in Eq. 1) of Stone's method. As we use all the *m* components for the fitting with Eq. 2, the obtained coefficients are thus "averaged" over *m* and related to the order L; they are denoted below as a_L and b_L.

As discussed previously [4], we also decided to consider, instead of the coordinate form (Eq. 3), a modified or "scaled" form:

$$R_L^m(A) = \sum_{i=1}^{N} Q_0^0(i)\, X_L^m(A, i) d_{iA}^{-K} \qquad (4)$$

which includes a term inversely proportional to the distance between the A atom and its *i* neighbor, $d_{iA} = ((X_i - X_A)^2 + (Y_i - Y_A)^2 + (Z_i - Z_A)^2)^{1/2}$, K being an empirical value whose choice should be discussed (see Discussion). Expressions for X_L^m can be found in Ref. 15. At this stage, let us just say that all the results we will present further for all the systems have been obtained with K = 2L +1.

Computational Aspects

T1 The EDs of the ALPOs (Table I) were computed with the CRYSTAL98 code [14] at various periodic DFT (PDFT) levels. The considered ALPOs were chosen owing to their "small" size elementary unit cell (UC) and relatively small number of AO per UC. Their initial X-ray diffraction (XRD) structures were optimized with the GULP code [18] and Catlow force field [19, 20]. The "Mulliken" AMMs up to the fourth order were calculated within the scheme developed by Saunders et al. [13] using the B3LYP, Perdew-Wang (PW91), and Perdew-Burke-Ernzerhof (PBE) functionals with the 6-21G** basis set (for shortness, noted below basis set 3 or BS3) for all ALPOs, while the ATN and ATO structures were also considered at other levels as STO-3G (BS1), 3-21G (BS2), and 8-511G*(Al)/8-521G*(P)/8-411G*(O) (BS4) for comparison. The ED at the Al-O and P-O bond critical points (3, –1) were evaluated with TOPOND [21]; they were found to be in satisfactory agreement with the experimental one obtained by Aubert et al. for berlinite [17] and AlPO$_4$-15 [22]. The density of valence atomic states (DOS) of the ATN structure was calculated with a shrinking factor of 8 in reciprocal space and compared with the experimental XPS spectrum of berlinite [23].

Results and Discussion

As we have demonstrated that the accurate calculation of the electrostatic potential (EP) in ALPOs requires at least a good approximation of the O dipoles $Q_1^m(O)$ and quadrupoles $Q_2^m(O)$ as well as of the Al octupoles $Q_3^m(Al)$ and P octupoles $Q_3^m(P)$ [4], we will limit the present analyses to these AMMs only. This importance of the P octupoles relative to the other phosphorus AMMs is coherent with the ratio of the multipoles fitted from the XRD experi-

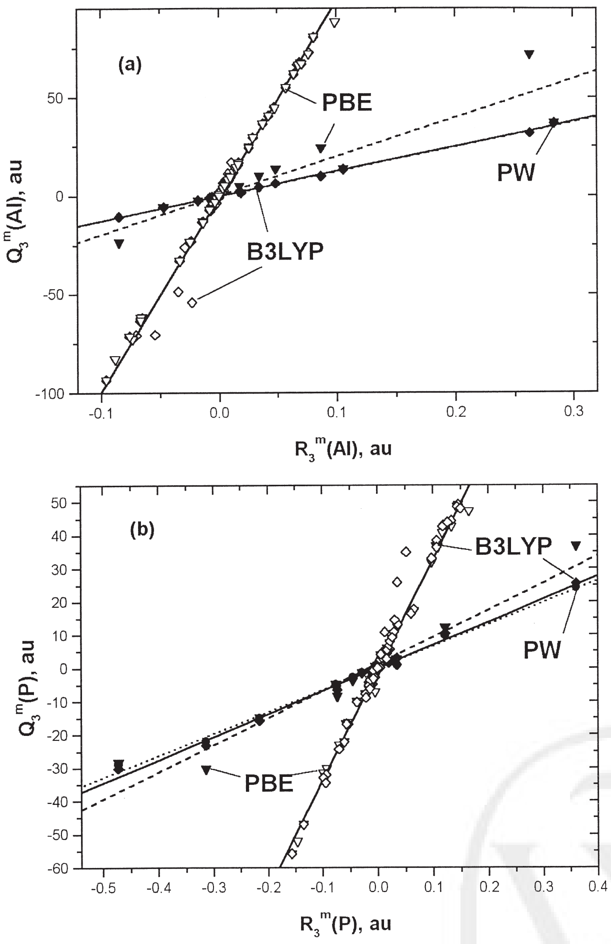

FIGURE 1. Octupole moments versus the cumulative coordinate for the Al (a, top) and P (b, bottom) atoms for all ALPOs calculated via the Mulliken partition with the B3LYP (diamonds), PW91 (circles), and PBE (triangles) functionals at the 6-21G** (BS3, open symbols) and 8-511G*(Al)/8-521G*(P)/8-411G*(O) (BS4, closed symbols) basis set levels and approximations (Eqs. 2, 4) for the B3LYP, PW91, and PBE functionals shown by solid, dotted, and dashed lines, respectively.

mental ED for dihydrogen phosphate [24], i.e., the absolute values of the largest Q_2^0(P), Q_3^{-2}(P), and Q_4^{-4}(P) components are 0.143, 2.420, and 0.893 au, respectively (table 6 in Ref. 24).

First, we mention that we succeeded in obtaining approximations of the octupoles Q_3^m at the Al and P atoms that are very accurate with both largest BS3 and BS4 basis sets (Fig. 1). F1 The fitted a_L and b_L constants using the ED calculated with B3LYP are presented in Table II T2 (the values with the other functionals are not reported, as they are very similar, with slightly worse results for PBE, as shown below). Let us note that b_L is always small, i.e., lower than its statistical error, so that it can be accepted as zero. The a_L value is thus the unique important parameter for each AMM of order *L*. Despite the fact that the correlations of the fit between the AMMs Q_L^m and cumulative coordinates R_L^m are already good for the XRD models of the ALPOs, we wish to add that preliminary optimization of their 3D structures improves the correlation and hence deserves a special remark. Indeed, previously [4], we did not note any serious difference between the fitting of the AMMs based on the XRD models, or on the structures optimized with the BKS force field (FF) [25]. However, this conclusion seems to have been the consequence of the relatively bad quality of the BKS FF used in our previous work [4]. More detailed analyses of a series of FFs indeed proved the bad fit of the AlO_4 geometry with the BKS FF [26]. The application of Catlow's FF [19, 20] improved the quality of the CC approximation, as noted for the O quadrupole in Table II; namely, the addition of AMM data (10 points) for the nonoptimized XRD berlinite model to the dataset of the ATN and ATO models optimized with Catlow's FF decreased the fit quality of Q_2^m(O) from $r^2 = 0.991$ to $r^2 = 0.951$. Unfortunately, in the case of berlinite optimized with Catlow's FF, no SCF convergence could be reached with BS4 at any functional level used herein, and thus one could not corroborate the close quality of the fitting based on the two smallest size optimized models.

The choice of the DFT functional is more important with the extended BS4 basis than with BS3, as shown by the fit of the Q_3^m(Al) and Q_3^m(P) values. If the B3LYP (diamonds in Fig. 1a,b) and PW91 (circles which coincide with the B3LYP diamonds in Fig. 1) calculations result in a similar accuracy (i.e., the approximations shown by solid and dotted lines for B3LYP and PW91, respectively, are very close), the AMMs computed with PBE and the BS4 basis (filled triangles approximated by dashed line in Fig. 1) are less precisely fitted. The lower quality can be easily visualized by the larger deflections of the PBE data (filled triangles) from the approximation (dashed lines).

Another important difference between the BS4 and BS3 basis sets was noted while fitting the AMMs at the O positions. The Q_1^m(O) dipole values calculated with the BS4 did not show any correlation at all using the CC "scaled" form (Eq. 4) with any functional, i.e., r^2 is around 0.2 or 0.3, the opposite of the Q_1^m(O) values calculated with BS3, which could be accurately fitted (Fig. 2a, Table II). Better, or at least acceptable, F2

TABLE II

Fitted parameters a_L, b_L, and correlation r^2 of Eq. 2 using all N *m* components (N = K × G, K is the number of all crystallographic independent A type atoms, G = 2L + 1) for the atomic multipole moments Q_L^m calculated via the Mulliken partition of the ALPO sieves at the BS3 and BS4 basis sets and B3LYP functional levels.

		6-21G** (BS3)				8-511G*(Al). . .(BS4)			
A	L	N	a_L	b_L	r^2	N	a_L	b_L	r^2
P[a]	3	84	332.1	−0.247	0.997	14	69.118	0.084	0.996
Al[b]	3	84	991.8	−0.585	0.991	14	126.3	−0.015	0.999
O	2	245	1.586[c]	-6.4×10^{-4}	0.901	40	−3.695[d]	1.8×10^{-3}	0.991
O	1	147	−0.811[e]	-1.6×10^{-4}	0.906	24	0.030[f]	-1.4×10^{-3}	0.693

[a] Figure 1b.
[b] Figure 1a.
[c] Figure 2b.
[d] If adding the XRD model of berlinite to the fitted set of the Q_2^m values: N = 50, $a_L = -3.238$, $b_L = 1.4 \times 10^{-3}$, and $r^2 = 0.951$.
[e] Figure 2a.
[f] Nonscaled CC coordinate (Eq. 3).

correlations for the O dipoles calculated at the BS4 level were obtained if the "nonscaled" CC form (Eq. 3) is applied, i.e., $r^2 = 0.643$, 0.693, and 0.741 for PBE, B3LYP, and PW, respectively.

In light of the importance of the O moments for the EP calculation, the bad accuracy of the O dipole fitting, i.e., even with the "nonscaled" CC form (Eq. 3) $r^2 = 0.693$ with B3LYP and BS4, might look problematic for the CC scheme [4]. Fortunately, this lower precision for the Q_1^m(O) approximation with BS4 is shown to be less important if one compares the roles of the dipoles and quadrupoles for the EP calculation with both basis sets as shown for the ATN sieve (Table III). Indeed, using the absolute values of the maximal AMM components, one can crudely evaluate the ratio of the respective terms of the multipole decomposition to the EP, for example, at positions of adsorbed/trapped molecules in the ALPOs. The intervals of the Q_1^m(O) values are very close to the BS3 (Fig. 2a) and BS4 basis sets, i.e., ±0.065 and ±0.07 au, respectively. The intervals for the Q_2^m(O) values are approximately ±0.22 au (Fig. 2b) and ±0.7 au (not shown for brevity) with BS3 and BS4, respectively. So, the modulus of the O quadrupole/dipole ratio rises from 3.4 to 10 with the basis set shift. The weights of the respective terms of the multipole decomposition to the EP could then be evaluated approximately as $3.4/r$ or $10/r$, the distance r between the framework O atom and a potential adsorption site being expressed in au. For example, at the observed experimental distance $r = 2.07$ Å (3.91 au, 1 au = 0.5292 Å) between the H of an adsorbed H_2O molecule and the framework O_6 atom of $AlPO_4$-15 [27], the dipole contribution to the total EP is comparable to the quadrupole one with BS3 ($3.4/r = 0.87$) and the O dipoles are accurately fitted (Fig. 2a). With BS4, the quadrupole/dipole ratio at the same position changes to $10/r = 2.56$, which corresponds to a less essential dipole term relative to the quadrupole one. So, the lower precision in the fitting of the Q_1^m(O) values is less important from a quantitative point of view. Its minor importance can also be illustrated by the calculation, using CRYSTAL, of the ratio between the EP values with and without Q_1^m(O); for example, in the Al-O_1-P plane of ATN, corresponding to the cavity wherein a sorbed molecule can be trapped, as done previously using AMMs calculated with PHF electron densities (fig. 7 in Ref. 4). The differences between the EP(3) values calculated with Q_1^m(O) and without Q_1^m(O) in the ATN cavity is around 10% with BS4 (upper right corner in Fig. 3a) and around 30% with BS3 (upper right corner in Fig. 3b). These results are in agreement with the increase of the quadrupole/dipole ratio of the EP terms from 0.87 to 2.56 upon shifting from BS3 to BS4. Let us note that very large EP differences are evidently observed along the iso-contour line EP(3) = 0 (line with –170% differences in Fig. 3b), but such a behavior is not physically important and is only a minor disadvantage of the EP differences. The sufficiency of the third-order AMMs at all atoms can additionally be proved by calculating EP differences relative to the EP(6) using all AMMs up to sixth order. Such (1 – EP(3)/EP(6)) ratios are within the range between –0.25 and 0.75% maximum (in absolute value) fluctuations within the same ATN cavity, while (1 – EP(4)/EP(6)) differ-

T3

F3

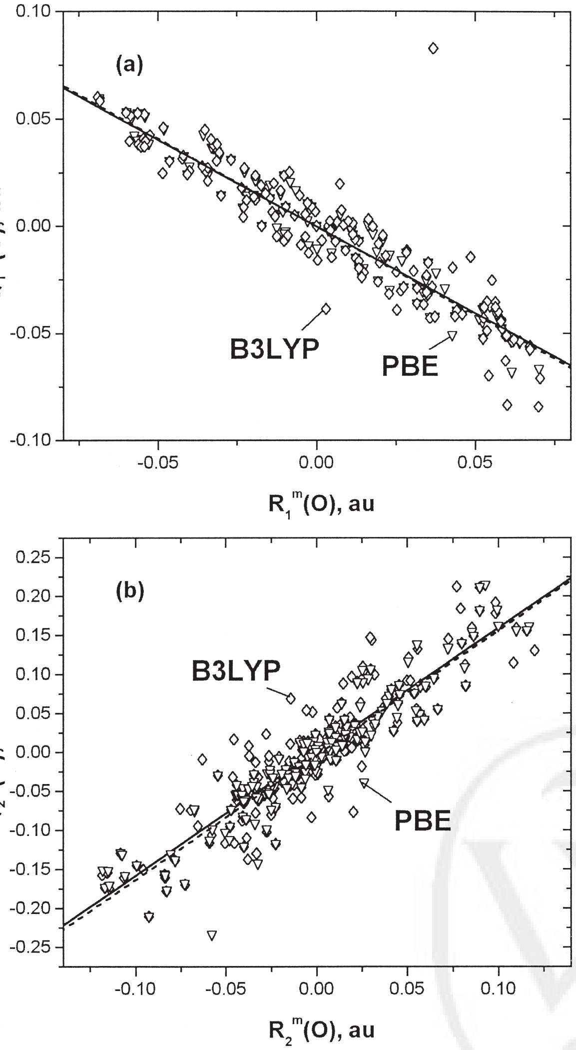

FIGURE 2. Dipole (a, top) and quadrupole (b, bottom) moments versus the cumulative coordinate for the O atoms of all ALPOs calculated via the Mulliken partition with the B3LYP (diamonds) and PBE (triangles) functionals at the 6-21G* basis set level (BS3) and approximations for the B3LYP and PBE functionals shown by solid and dashed lines, respectively.

ences are between −0.25 and +0.12% (note: figures are not shown for brevity). Finally, let us add that AQ: 1 the lower accuracy for the AMMs which contribution terms to the EP are small is a characteristic of the CC method. Indeed, T dipoles (T = Al, Si, P) are either not allowed at the strictly tetrahedral TO_4 site or are very small for the usual TO_4 distortions, in agreement with the experimental evaluations for tetrahedral sites [24].

The variation of the characteristics of the ED with the basis sets, as shown above via the quadrupole/dipole ratio, is accompanied by a redistribution of the ED not only between the oxygen AMMs, but also between the AMMs of all other constituting elements of the framework. The absolute values of the most important components of the AMMs for the ATN sieve computed with the B3LYP functional at the four different basis set levels from minimal BS1 to BS4 are given in Table III. If one compares the AMM values from the minimal to the most extended basis, an encouraging similar behavior is noted for the AMMs (Table III) and the Mulliken charges (Table IV, Fig. 4). Both the AMMs F4 and the charges obtained at the upper level basis set approach the BS1 values (Tables III, IV). Even if this behavior cannot really be characterized as a convergence, let us mention that it has been noted for the atomic charges for all-siliceous zeolites [6, 7, 12]. With the improvement of the basis set, the absolute charge values increase with BS2, then drop with BS3, and finally again approach the BS1 values with the most extended BS4 basis. Additionally, in Figure 4 we also report the approximated O charges (closed symbols) as obtained via a three-dimensional dependence:

$$Q_0^0(R, \Delta R, \vartheta) = c_1 e^{nR} + c_2 e^{m(\Delta R - R_0)} \times \cos(\vartheta - \vartheta_0) \tag{5}$$

the average T-O distance being R = 1/2×(|Al-O|+|P-O|), the bond difference ΔR = |Al-O|-|P-O|, the angle ϑ = Al-O-P, and c_1, c_2, n, m, R_0, and ϑ_0 being fitted parameters [8]. The difference between the charges of the different crystallographic O types for a given T-O distance, for example, between the ones given by open triangles for BS2 in Figure 4, illustrates the O charge fluctuation with respect to the two other ϑ and ΔR coordinates, which are not shown in Figure 4. It can also be clearly seen that the variation with respect to the ϑ and ΔR changes when varying the basis set level is emphasized the most at the BS2 level. This illustration suggests, moreover, that both the 3D dependence (Eq. 5), as proposed before [8], and the CC approach (Eqs. 2–4) could be used together within a unified approach which would allow one to simulate the set of all important AMMs needed for the calculation of the EP of any ALPO structure on the basis of its geometry only. Starting from the O charges and using dependences analogous to Eq. 5 for the Al and P charges, one can get high-order AMMs via Eqs. 2–4, whose parameters would be fitted using a set of small size systems of similar chemical composition.

TABLE III

Absolute values of the atomic multipole moments $|Q_L^m(A)|$ calculated via the Mulliken partition for the ATN sieve at different basis set levels with the B3LYP functional.

A	L, m	STO-3G (BS1)	3-21G (BS2)	6-21G** (BS3)	8-511G*(Al) (BS4)
P	3, −3	24.60	5.151	47.02	30.14
Al	3, −3	16.05	4.904	29.50	13.38
O_1	2, −2	0.5494	0.9344	0.1556	0.7223
O_2	2, −2	0.0739	0.2077	0.0327	0.1580
O_3	2, −2	0.2859	0.2657	0.1057	0.0841
O_4	2, −2	0.2104	0.3310	0.0867	0.2083
O_1	1, −1	0.0345	0.0245	0.0001	0.0724
O_2	1, −1	0.0341	0.0036	0.0236	0.0516
O_3	1, −1	0.0875	0.0117	0.0362	0.0337
O_4	1, −1	0.0185	0.0135	0.0006	0.0436

This similarity of the behavior of the Mulliken charges and high-order AMMs is really apparent when looking to the important $a_2(O)$ coefficient. The $a_2(O)$ values, i.e., the slope of the approximations, calculated as –3.695 au with BS4 (not shown here for brevity) approaches the BS1 value of –3.058

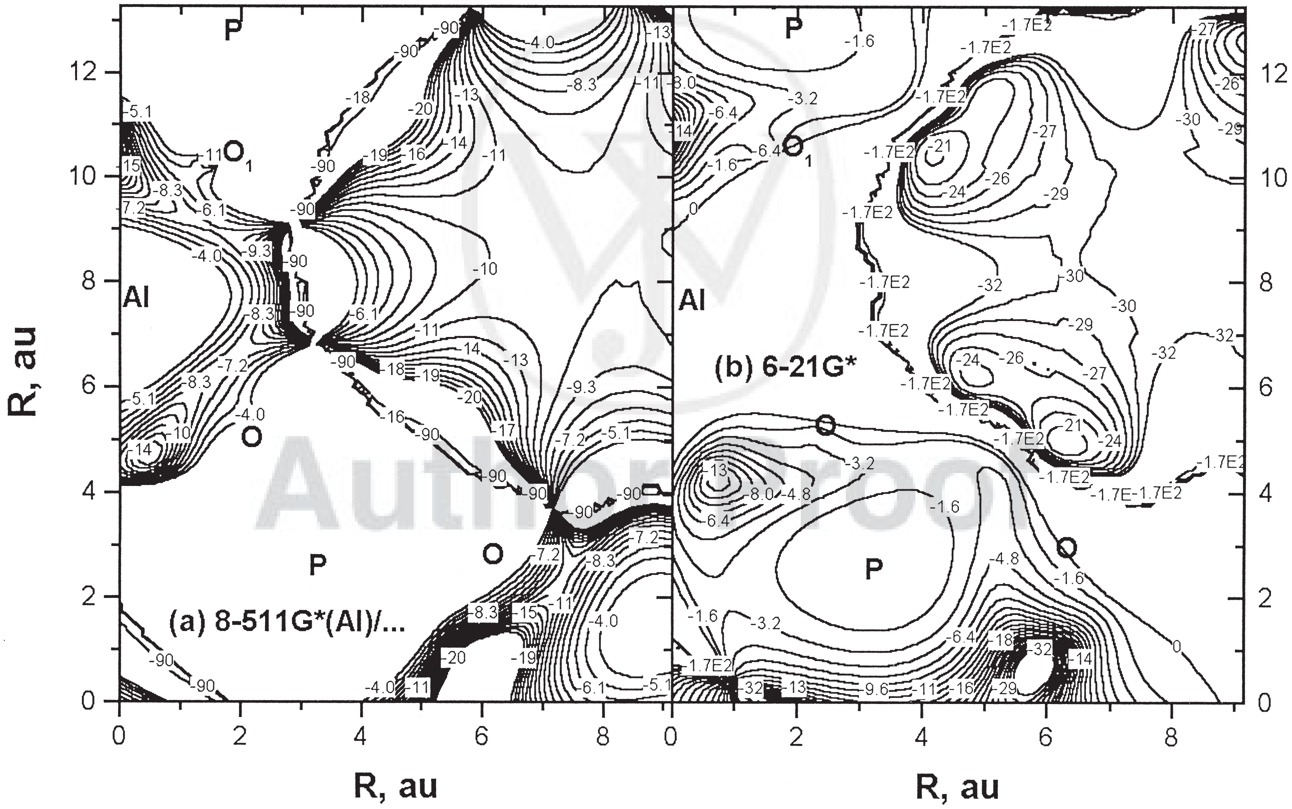

FIGURE 3. Electrostatic potential (EP) iso-contour differences (1 – EP'(3)/EP(3))×100 (%) between the EP'(3) computed allowing all moments up to third order on all atoms with exception of $Q_1^m(O)$ relative to the potential representation EP(3) also including $Q_1^m(O)$ in the Al-O_1-P plane (distances in au) of the ATN framework calculated with B3LYP at the (a, left) 8-511*(Al)/8-521*(P)/8-411*(O) (BS4) and (b, right) 6-21G** basis set levels (BS3). Atomic sites are depicted also for the atoms above/below the plane.

TABLE IV

Atomic charges (e) calculated via the Mulliken partition for the ATN sieve at different basis set levels with the B3LYP functional ($Q_0^0(O_{aver}) = \sum_i n_i \times Q_0^0(O_i)/\sum_i n_i$).

X	STO-3G (BS1)	3-21G (BS2)	6-21G**(BS3)	8-511G*(Al)/..(BS4)
P	1.428	2.161	0.761	1.274
Al	1.116	1.466	0.390	1.298
O_1	−0.640	−0.917	−0.293	−0.648
O_2	−0.639	−0.910	−0.291	−0.643
O_3	−0.627	−0.890	−0.274	−0.632
O_4	−0.639	−0.910	−0.293	−0.648
O_{aver}	−0.636	−0.907	−0.288	−0.643

au in the $a_2(O)$ sequence for all four basis sets, i.e., –3.058, –5.136, 1.586, and –3.695 au from the minimal one to the extended basis. In addition, the coherence between the variations of the average O_{aver} charges (last line of Table IV) and the coefficients $a_2(O)$ with the basis sets can be even better visualized considering the charges and $a_2(O)$ values in a reduced form, i.e., divided by the minimal absolute values $(Q_0^0(O_{aver}))_{min}$ and $(a_2(O))_{min}$ in the series of the four basis sets. Both minimal absolute values correspond to BS3, i.e., 1.586 for the $a_2(O)$ and −0.288 for $Q_0^0(O_{aver})$ (Table IV). Then, the $|Q_0^0(O_{aver})/\ (Q_0^0(O_{aver}))_{min}|$ and $|a_2(O)/(a_2(O))_{min}|$ values are 2.21 / 3.15 / 1 / 2.23 and 1.93 / 3.24 / 1 / 2.33, respectively, for all four bases starting from the minimal to the extended one.

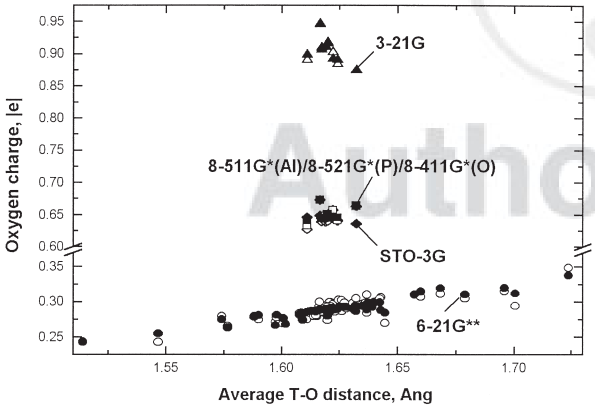

FIGURE 4. Atomic charges of the O atoms calculated via the Mulliken partition (open symbols) and approximated with a 3D dependence (closed symbols) versus the average T-O distance R = 1/2×(|Al-O|+|P-O|) (Eq. 5) at the STO-3G (BS1, diamonds), 3-21G (BS2, triangles), 6-21G** (BS3, circles), and 8-511G*(Al)/8-521G*(P)/8-411G*(O) (BS4, squares) basis set levels using B3LYP.

The behavior of the a_L values in the approximations of the AMMs, however, cannot be characterized as a real "convergence" with respect to the improvement of the basis set. The BS1 AMM values do not exactly coincide with the ones obtained with BS4 (Table III). In the case of the oxygen AMMs, the a_1 and a_2 values change signs with the basis set shift (Table II). A similar a_1 sign inversion between BS1 and BS3 was also observed in all-siliceous zeolites (fig. 4a,b of Ref. 4). The most important issue is that despite the variation of the AMMs for each atom type with different basis sets, we can fit the a_L parameters for all important AMMs for each basis set (Figs. 1, 2).

The closeness between the charges and the high AMMs calculated with BS1 and the ones calculated with BS4 results in the smallest EP differences compared to the respective EP differences obtained with BS2 or BS3. For example, in Figure 5a we report EP iso-contour values and differences calculated using all AMMs up to the sixth order obtained with the most extended basis in the Al-O_1-P plane of ATN (as in Fig. 3). The differences between the EP values calculated with BS1 and BS4 (Fig. 5b) do not exceed 32% in the ATN cavity (upper right corner in Fig. 5b). Respective differences (1 – EP(6, BS2)/EP(6, BS4)) (Fig. 8c) and (1 – EP(6, BS3)/EP(6, BS4)) (Fig. 5d) are twice as large in absolute value, i.e., around −60 and 64%, respectively (upper right corners in Fig. 5c,d), thus resulting in over- and underestimation, respectively, of the EP calculated with BS4 in the ATN cavity. Large differences, for example, with BS1, as (1 – EP(6, BS1)/EP(6, BS4)), are again observed along the iso-contour line EP(6, BS4) = 0 (line with –130% in Figure 5b).

We think that these different trends of the EP with the basis set could result in practical advice for QM/MM approaches in which one combines basis sets and/or theory levels for the QM cluster and the

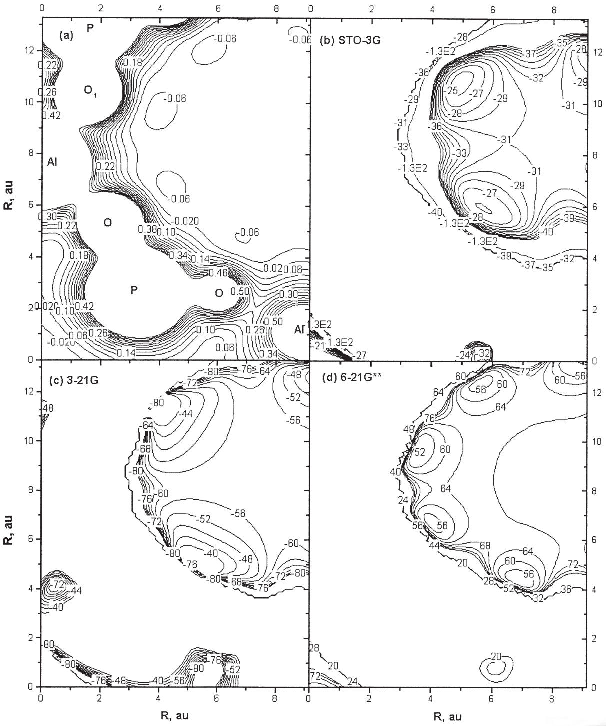

FIGURE 5. (a) Electrostatic potential (EP) iso-contour values (au) in the Al-O_1-P plane (distances in au) of the ATN framework calculated with B3LYP at the extended 8-511*(Al)/8-521*(P)/8-411*(O) basis set (BS4) level. b–d: EP iso-contour differences presented as (1 – EP(6, basis set)/EP(6, BS4)×100 (%) obtained using (b) STO-3G (BS1), (c) 3-21G (BS2), and (d) 6-21G* (BS3) relative to the EP(6, extended) potential allowing all AMMs up to sixth order. Atomic positions are depicted in (a).

outer MM part [2]. The choice of the basis set for the "remote layers" as classified for the MM part in ONIOM [2] should evidently be done by taking into account the nature of the properties which should be precisely calculated, i.e., frequencies, adsorption potential, etc. Should the electrostatic effects be of primary importance, then a basis set of a priori poor quality such as BS1 could be more useful versus the more accurate BS2 or BS3 bases. BS1 provides a better EP representation of the EP components produced by the remote layers at the central QM part, when the latter is treated at the BS4 level.

Regarding the question of the best quality basis set used herein for the AMMs calculation, one also cannot ignore the important inversion of the charges $Q_0^0(P) = 1.274$ e $< Q_0^0(Al) = 1.298$ e observed with the extended BS4 basis with respect to all other bases of lower quality (Table IV). At first glance, the smaller P charge as compared to Al with BS4 is contrary to common good chemical sense, and thus would require a further verification. But we first note that the same inversion has been obtained by fitting high-resolution electron density measurements for two P atoms (1.29 and 1.31 e) and two Al at the hexagonal sites (1.59 and 1.62 e) in the $AlPO_4$-15 sieve containing H_2O and NH_4^+ [27]. The second argument for the possible $Q_0^0(P) < Q_0^0(Al)$ ratio comes from the assignment of chemical ^{29}Si shifts at various nSi(4-n)Al positions in NaY [28], where an analogous ratio between the Si (between 1.33 and 1.41 e) and Al (2.015 e) charges was obtained. The $Q_0^0(Si) < Q_0^0(Al)$ obtained in Ref. 28, however, cannot serve directly for our ALPO case, while the results of Ref. 27 refer to hexagonal Al sites. Even if neither of the two reported studies [27, 28] can thus really ascertain the order of the atomic charges calculated at the BS4 level, we believe that the small difference between $Q_0^0(P)$ and $Q_0^0(Al)$ cannot serve to discriminate between the basis sets.

Trying to verify the application of the CC technique to other schemes of electron partition, we also used the Bader scheme as implemented in TOPOND [21]. A successful fitting of the dipole and quadrupole Bader moments at the O positions (AMMs of higher orders are not available within the code) will be discussed elsewhere, but here we would like to mention that Bader charges in the case of ATN provide a ratio $Q_0^0(P)/Q_0^0(Al) > 1$ with both the BS3 and BS4 bases at the B3LYP level (Table V). The minor charge differences between T5 the different O types are not coherent between the Mulliken and Bader schemes; we just note that the largest O charge calculated with BS3 corresponds to the O_3 type with both electron partitions (Table V).

Finally, in order to test the quality of the respective basis set, we used a qualitative analysis of the density of valence states (DOS) calculated with all different basis sets for ATN, ATO, and berlinite, an experimental XPS spectrum being available for berlinite [23]. In that case, it is well known that both HF and DFT methods cannot provide accurate values for the gap between the occupied and empty states, but the width of the upper valence bands can be compared with the experimental one [23, 30]. In the absence of precise XPS values (fig. 2 in Ref. 23 does not include precise values), one will only describe approximately the experimental spectrum which includes two massifs with two peaks each and which expands over 0.44 E_h (12 eV) [23]. The intensity of the lower energy massif is twice as large as that of the higher one. Evidently, the calculated Fermi level is different for each basis set, i.e., −0.2

TABLE V

Bader[a] and Mulliken type charges (e) for the ATN sieve.

	6-21G** (BS3)				8-511G*(Al)/. . . (BS4)			
	Bader	B3LYP	PW	PBE	Bader	B3LYP	PW	PBE
P	3.999	0.761	0.761	0.762	3.979	1.274	1.253	1.248
Al	2.565	0.390	0.392	0.387	2.573	1.298	1.289	1.287
O_1	−1.639	−0.293	−0.292	−0.291	−1.645	−0.648	−0.641	−0.639
O_2	−1.642	−0.291	−0.291	−0.289	−1.646	−0.643	−0.645	−0.634
O_3	−1.636	−0.274	−0.277	−0.275	−1.646	−0.632	−0.626	−0.624
O_4	−1.642	−0.293	−0.295	−0.293	−1.645	−0.648	−0.640	−0.639

[a] Calculated with TOPOND [21] at the B3LYP level.

E_h with BS1, −0.236 E_h with BS3, −0.276 E_h with BS4, and −0.304 E_h with BS2. So, one could assign a different sketched DOS of ATN (Fig. 6a) to the observed XPS spectra of berlinite (upper left window of Fig. 6a) shifting the respective Fermi level for each basis set.

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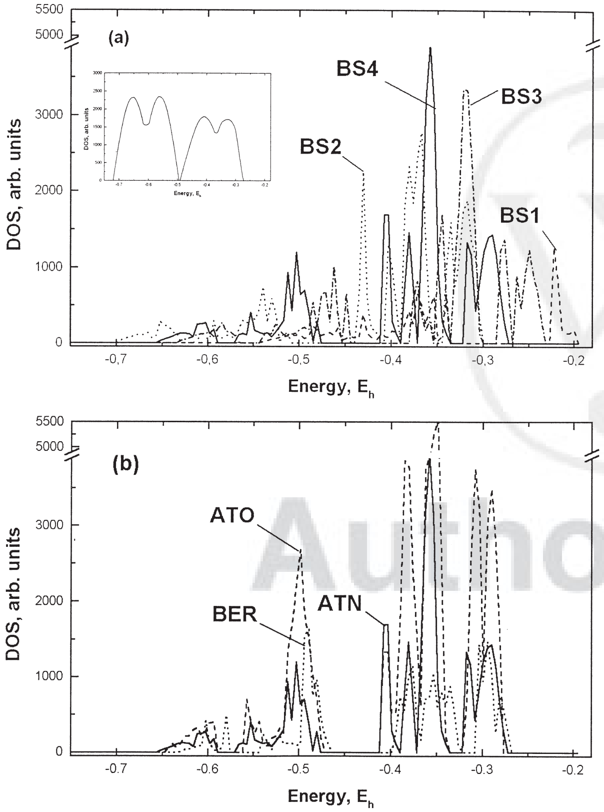

FIGURE 6. Density of valence atomic states (DOS) for (a, top) the ATN structure with the BS1 (dashed line), BS2 (dotted line), BS3 (dotted dashed line), and BS4 (solid line) basis sets and for (b, bottom) the ATO (dashed line), ATN (solid line), and berlinite (BER, dotted dashed line) structures with the BS4 basis set (1 E_h = 27.2 eV) using B3LYP functional.

First, we checked that all three ALPOs (berlinite, ATO, ATN) with totally different atomic geometries (bond lengths, Al-O-P angles) have DOS peaks calculated at the BS4 level nearly in the same energy range (Fig. 6b), i.e., from −0.27 to around −0.65 E_h. Then we calculated the DOS of ATN to compare it with the experimental one of berlinite (Fig. 6a). The earlier theoretical simulations of the DOS for berlinite [23, 30] resulted in a lower intensity for the left massif, which is in accordance with our DOS calculated for ATN with all basis sets or ATO and berlinite with the most extended one, but this is contrary to the experimental one for which the left massif is higher than the right one [23]. The DOS width of ATN is coherent between all basis sets with the exception of BS1. In the latter case, the left and right massifs are separated by a too wide energy gap, i.e., 0.12 E_h, as compared to 0.08 E_h for BS2 and 0.07 E_h with the other bases. BS1 also results in a narrower width of the valence DOS band, i.e., 0.35 E_h, as compared to the experimental one, i.e., 0.44 E_h, while the bands possess intermediate widths around 0.38 E_h with the other basis sets. So, the comparison of the positions of calculated DOS and experimental XPS spectrum cannot discriminate between any of the BS2, BS3, and BS4 basis sets.

Conclusions

The electron density (ED) and atomic multipole moments (AMMs) for several aluminophosphates (ALPOs) and berlinite were computed with the CRYSTAL98 code at various periodic density functional theory (PDFT) levels, i.e., B3LYP, PW91, and PBE, and different basis sets, i.e., STO-3G (BS1), 3-21G (BS2), 6-21G** (BS3), and 8-511G*(Al)/8-521G*(P)/8-411G*(O) (BS4). To approximate the AMMs at all the various PDFT levels, we applied a cumulative coordinate (CC) technique proposed at the periodic Hartree-Fock level [4]. This technique allows one to approximate the most important AMMs by linear functions with one important regression coefficient, a_L, for all the components of the AMM of order L for all the different crystallographic atom types (i.e., O, Al, Si, H). In the case of the most extended BS4 basis set, the a_3(Al), a_3(P), and a_2(O) coefficients corresponding to octupole of Al, octupole of P, and quadrupole of O, respectively, are accurately fitted, while BS3 allows such a level of precision for a wider series of coefficients, i.e., a_3(Al), a_3(P), a_1(O), and a_2(O). The difference between ALPOs and all-siliceous systems is that the BS3 basis set results in the lowest absolute charge values on all the ALPO atoms.

Electrostatic potential (EP) iso-contours were calculated and compared for the series of four basis sets at locations available for adsorbed/trapped molecules. No EP convergence with the basis set was observed. The contribution of the O dipoles to the EP values were shown to vary strongly between BS3 and BS4 bases. The application of this last basis set results in a poorer correlation of the O dipole with all three PBE, PW91, and B3LYP functionals, which correlates with a decrease of the relative dipole contribution to the EP values. An alternative (nonscaled) form of the approximate function for the O dipole was satisfactory in the a_1(O) evaluation case with BS4. The EP contribution of the O quadrupole moments increases at the most extended basis level, which correlates with a more precise a_2(O) evaluation. The CC fitting of the O quadrupole moments calculated with the extended basis set is more accurate ($r^2 = 0.991$, Table III) as compared to the one calculated with BS3 ($r^2 = 0.901$, Table III) or the one computed with the PHF approach (for example, fig. 5b in Ref. 4). As a result of the same range of the Mulliken charge values, the closest coincidence of the calculated EP value is observed between the extended BS4 basis and the minimal STO-3G one. The similarity between the charges calculated at the two levels resembles the convergence observed earlier for all-siliceous systems [6, 12].

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AQ1: please clarify sense.

AQ2: no figure 8; fig. 5c?

AQ3: have journal name, year, vol, and pp?

AQ4: have year, vol, and pp?