# Cost-Effective Quantum Mechanical Approach for Predicting Thermodynamic and Mechanical Stability of Pure-Silica Zeolites

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S Supporting Information

ABSTRACT: Several computational techniques for solid-state applications have recently been proposed to enlarge the scope of computer simulations of large molecular systems. In this contribution, we focused on two of these, namely, HF-3c and PBEh-3c. They were recently proposed by the Grimme's group, as "low-cost" ab initio-based techniques for electronic structure calculation of large systems and were proved to be effective essentially for organic molecules. HF-3c is based on a Hartree−Fock Hamiltonian with a minimal Gaussian quality basis set, whereas PBEh-3c is a density functional theory (DFT) based method with a hybrid functional and a medium-quality basis set. Both HF-3c and PBEh-3c account for dispersion (London) interactions and are free from the basis set superposition error due to limited basis set size, through several pairwise semiempirical corrections. To the best of our knowledge, despite the promising results on the cost-accuracy side of molecular simulations of organic molecules, these methods have been used only in few cases for solid-state applications. In this contribution, we studied the performance of HF-3c and PBEh-3c for predicting the properties of inorganic crystals to enlarge the applicability of these cheap and fast methodologies. As a testing ground, we have chosen a well-known class of material, e.g., microporous all-silica zeolites. We benchmarked geometries, formation energies, vibrational features, and mechanical properties by comparing the results with literature data from both experiment and computer simulation. For structures, HF-3c is extremely accurate in predicting the zeolites cell volume, albeit we do not include any vibrational contribution, neither zero point nor thermal, on the computed volumes, which may introduce small variations in the predicted values. For the energetic, the relative stability of the zeolites using the DFT//HF-3c approach allows predictions within the experimental error for most of the cases taken into consideration when the experimental enthalpies were corrected back to electronic energies by using the HF-3c thermodynamic contributions computed in the harmonic approximation. This strategy is particularly convenient, as the slow step (geometry optimization) is carried out with the cheapest HF-3c method, whereas the fast step (single point energy evaluation) is carried out with costly DFT methods. In this sense, the use of the DFT//HF-3c approach results to be a promising one to predict the stability and structure of microporous materials. Finally, the HF-3c method predicts the mechanical properties of the zeolite set in reasonable agreement with respect to those computed with the state-of-the-art DFT simulations, indicating the HF-3c method as a possible technique for the mechanical stability screenings of microporous materials.
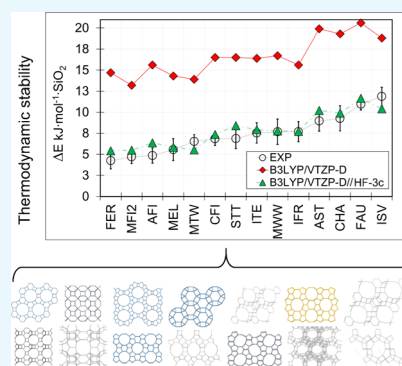
INTRODUCTION

In last years, we have witnessed the development of several computational techniques for solid-state (SS) applications that enlarged the possibility of computer simulations in this research field. Various wave-function-based approaches, earlier available for molecular systems only, docked on SS realm. Nowadays, we can use the golden standard for molecular simulation, e.g., coupled cluster with a full treatment singles and doubles, for systems with periodic boundary conditions, albeit with very large cost and small system size.[1−3] Moreover, the simulation of solids within the second-order Moller−Plesset approximation (MP2)[4] can be done routinely, albeit with serious limitations in terms of geometry optimization.[5,6] Furthermore, recent advances in accuracy and speed-up of the diffusion quantum Monte Carlo have appeared in recent work.[7] The above method includes electron correlation in a

formally correct manner. Therefore, they are accurate but computationally expensive, with a narrow range of applicability in material science, particularly as far as the system size is concerned, limiting their applicability to complex and more challenging systems.

For a routine simulation, a SS scientist can rely on density functional theory (DFT), in which electron correlation is included in the exchange and correlation potential (U_{XC}). In its simpler expression, it depends linearly on the electron density, but the accuracy of this flavor of DFT is not enough for chemical applications. Introducing the density gradient and/or part of exact Hartree−Fock (HF) exchange into U_{XC} increases
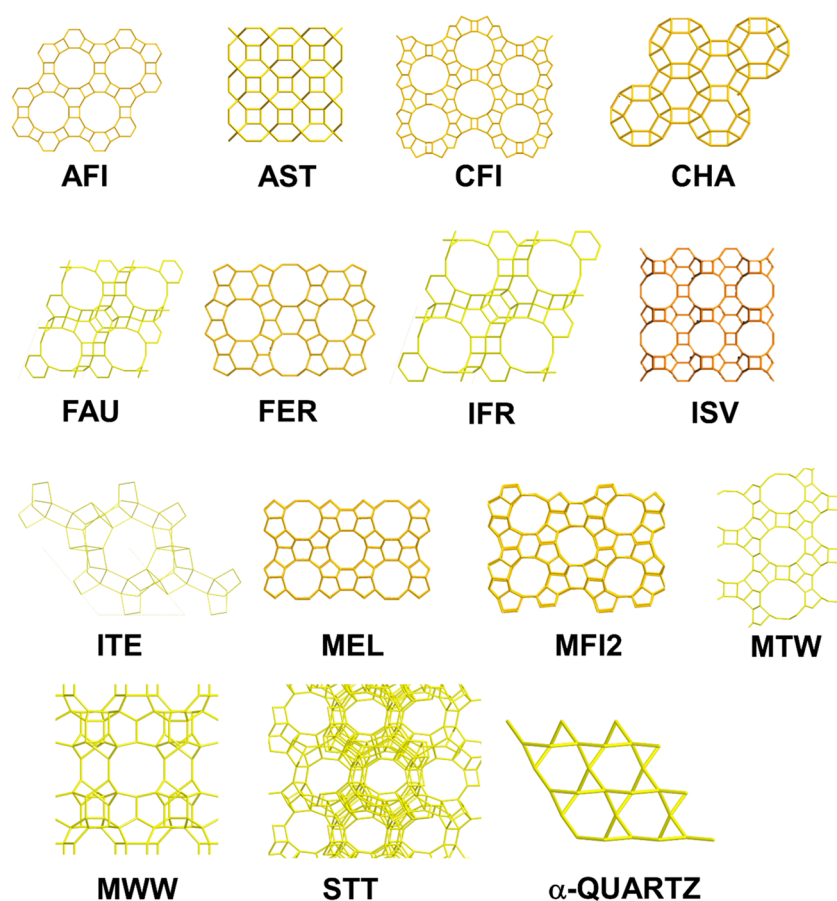
Figure 1. Set of the all-silica polymorphs studied in this work. Only the Si framework is shown.

the accuracy of DFT, and it can be applied for a variety of problems of chemical nature.[8−10] Including also the description of dispersion forces,[11] DFT simulation can reach in some cases, with a precise choice of parameters, the celebrated "chemical accuracy".[12]

Faster alternatives to DFT are semiempirical (SE) methods, which are based on highly approximated HF Hamiltonians, thus enlarging dramatically the investigable system size. Successful examples of these methodologies are the PM6 method,[13] along with the available refinements for an accurate description of H bonding and dispersion forces (PM6-D3H4)[14] and for halogenated systems PM6-D3H4,[15] as well as the more recent PM7.[16] Very recently, a semiempirical tight binding (TB) method for the noncovalently large bonded systems has been proposed, e.g., geometry, frequency, noncovalent, extended TB.[17] Unfortunately, to date, it is coded for molecular system only. In general, SE methods are not accurate enough when compared to standard DFT simulations as, for systems outside the molecular training set, they may experience large errors in the computed properties.

Recently, Grimme's group proposed a "low-cost" ab initio-based technique for electronic structure calculations that lies between the DFT and SE methods. Called HF-3c,[18] the method is based on a Hartree−Fock (HF) calculation with a minimal Gaussian-type basis set (MINIX). Thanks to three-atom pairwise semiempirical corrections, it exhibits the following features: (i) it is mainly free of basis set superposition error,[19] (ii) it accounts for dispersion (London) interactions,[20] (iii) it correctly computes the interatomic distances, despite the adopted minimal basis set.[18] Later on,

three other members joined the family of the "3c" methods, e.g., PBEh-3c,[21,22] HSE-3c,[21] and B97-3c.[23] The PBEh-3c and HSE-3c methods are DFT-based methods with a hybrid functional and a double zeta Gaussian-type basis set quality. Conversely, the B97-3c is a generalised gradient approximation (GGA) functional with a larger triple zeta with one polarization function (TZP) basis set. To the best of our knowledge, this promising 3c method family has only been applied to organic molecular systems in gas phase, solution, and solid state to date.[5,18,19,21−25] Our aim is to check the range of applicability of these methodologies up to the broad class of inorganic and composite materials.

In this contribution, we focused on two representative methods for this low-cost class of methods, e.g., HF-3c and PBEh-3c, to investigate several inorganic crystalline materials. As a benchmark for inorganic systems, a well-known class of materials, e.g., microporous materials, was chosen. We considered a set of pure silica zeolites recently studied by Román-Román et al.[26] Zeolites have found a widespread use in the field of catalysis, gas separation, and ion exchange.[27] Therefore, being able to model their features has important consequence in terms of applications.

We have relaxed the geometry and computed the relative stability and the mechanical properties of a set of zeolites. Our theoretical findings are compared with experiments and previously published theoretical values where available. We have also tested the dispersion-corrected density functional theory (DFT-D)//HF-3c-027 recipe in which the energy is estimated at the DFT-D level on the geometry relaxed with a revised version of the HF-3c approach. This approach was

proven to be cost-effective for computing energies and geometries of molecular crystals[5] and protein conformations.[28]

RESULTS AND DISCUSSION

Zeolite is a family of crystals with a microporous structure. Pure silica zeolites (SiO_2 polymorphs) can have a potential infinity variety of tetra-coordinated open-framework arrangements, with α-quartz as the thermodynamically most stable polymorph. In this contribution, we considered 15 silica polymorphs, e.g., a set of 14 zeolites and the α-quartz crystal, see Figure 1.

Unit Cell Volume Analysis. We have fully relaxed the cell and internal parameters of all sets with plain and scaled HF-3c and PBEh-3c methods by exploiting in full the crystal symmetry. As a comparison, we reported also the results of the PBE0-D2/VTZP and B3LYP-D2/VTZP methods, taken from ref 26. As a comparison with the hybrid DFT functionals taken from literature, we also tested the performances of the pure GGA PBE-D2/VTZP method.

The percentage deviation of the computed cell volumes with respect to experiments is graphically reported in Figure 2. The
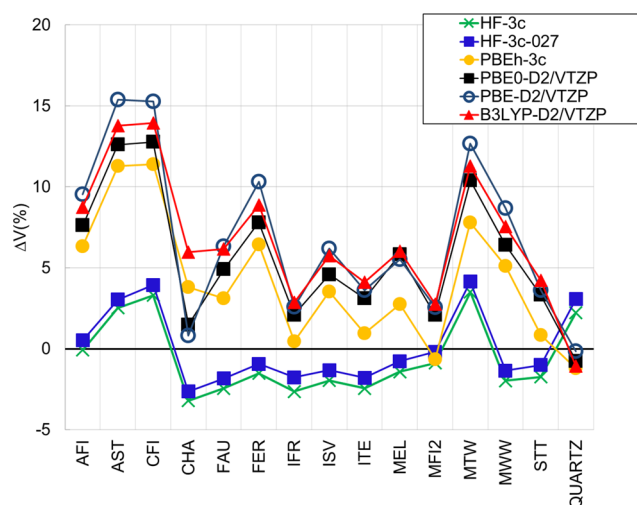

Figure 2. Percentage deviation from experiment of the computed volumes at the B3LYP-D2/VTZP,[26] PBE0-D2/VTZP,[26] PBE-D2/VTZP, HF-3c, HF-3c-027, and PBEh-3c levels of theory, for the silica polymorphs set.

HF-based methods outperform the DFT ones. Indeed, both plain and scaled HF-3c methods are in very good agreement with the experiments. The mean absolute percentage error (MARE) computed for the HF-3c and the HF-3c-027 methods is 2.1 and 1.9%, respectively (see Table 2). The standard deviation (SD) in both cases is 2.3%. Conversely, the best-performing DFT-based method, e.g., PBEh-3c, has only a MARE of 4.4% with a SD of 3.9%. Interestingly, the general trend in the volume prediction seems to correlate with the percentage of HF exchange in the functional definition. Indeed, the mean relative error (MRE) has the following trend Perdew−Burke−Ernzerhof (PBE) > B3LYP > PBE0 > PBEh-3c > HF (Table 1), in line with the increment of the exchange HF percentage, which is 0, 20, 25, 42, and 100%, respectively.

The theoretical framework (electronic energy relaxation) used to estimate the unit cell volume does not include any vibrational contribution, neither zero point nor thermal. The results obtain in such away are compared to the experimental

Table 1. Statistical Deviation (%) from the Experiments of the Computed Unit Cell Volumes for the Silica Polymorphs[a]

	MRE	MARE	SD%
HF-3c	−0.6	2.1	2.3
HF-3c-027	0.1	1.9	2.3
PBEh-3c	4.1	4.4	3.9
PBE0-D2/VTZP[26]	5.6	5.7	4.0
PBE-D2/VTZP	6.9	6.9	5.0
B3LYP-D2/VTZP[26]	6.7	6.9	4.1

[a]The formal definitions of the statistical function used in this table are reported in the Supporting Information.

data collected at room temperature (RT). To have a fair comparison between theory and experiments, one should quantify the effect of vibrations (at RT) on the unit cell volume size predicted by electronic energy relaxation. For that purpose, a quasi harmonic approximation (QHA) as implemented in CRYSTAL17 can be used. Unfortunately, QHA simulations are extremely costly, as they consist of a series of geometry optimizations at constant volume followed by frequency calculations. Therefore, we explicitly run QHA for α-quartz only using the PBE/VTZP-D2 level of theory. The unit cell volume change is about +1.4%. For zeolites, we relied on literature data run with force fields specifically derived for silica materials. Gale reported a cell volume contraction at $T = 200$ K for zeolite-A of 0.63%, whereas Faujasite reported even smaller value.[29] In a similar study, the volume variation in the $T = 50−300$ K range was computed to be −0.36% for zeolite-L, 0.39% for cancrinite, 0.31% for zeolite-X, and 0.06% (from 20 to 296 K) for experimental measurement on Al-exchanged zeolite-X.[30] As one can see, for zeolites, the expansion can also be negative as a function of the framework. Due to the very small absolute variation, we do not believe this effect will alter the main conclusion of the present work, as variations in volume as a function of adopted Hamiltonian are larger than the thermal effect.

Thermodynamic Stability. The enthalpy of formation (ΔH) of a material is the sum of three energy differences (with respect to the reference), e.g., electronic, vibrational zero point (ZPE), and thermal effect. Therefore, we corrected the experimental ΔH (298.15 K)[31,32] with vibrational ZPE and thermal energies computed at the HF-3c-027 level, thus obtaining a "quasi-experimental electronic energies of formation" directly comparable with the computed electronic energies. We scaled the HF-3c-027 (full IR spectra are reported in Figure S2) frequencies by 0.8707 (which affects the ZPE only). This factor minimizes the RMSD of HF-3c-027 frequencies with respect to those computed at the B3LYP/SVP-D* level for the α-quartz case. Interestingly, the applied scaling factor is very similar to the one recommended (0.87) in the original HF-3c publication.[18] The HF-3c-027 ZPE and thermal energy sum is similar for all zeolites, e.g., 2.3 ± 0.3 kJ mol^{-1} per SiO_2 unit (ME ± SD). Therefore, we propose to subtract 2.3 kJ mol^{-1} per SiO_2 unit as a simple and general procedure to compute "quasi-experimental ΔE" from the experimental ΔH values.

We have graphically resumed the computed energy of formation of the zeolite set in Figure 3 and compared it with the "quasi-experimental energy" of formations. A comprehensive statistical analysis is reported in Table 2. All energetic data are fully reported in Table S4. In contrast with the cell volume
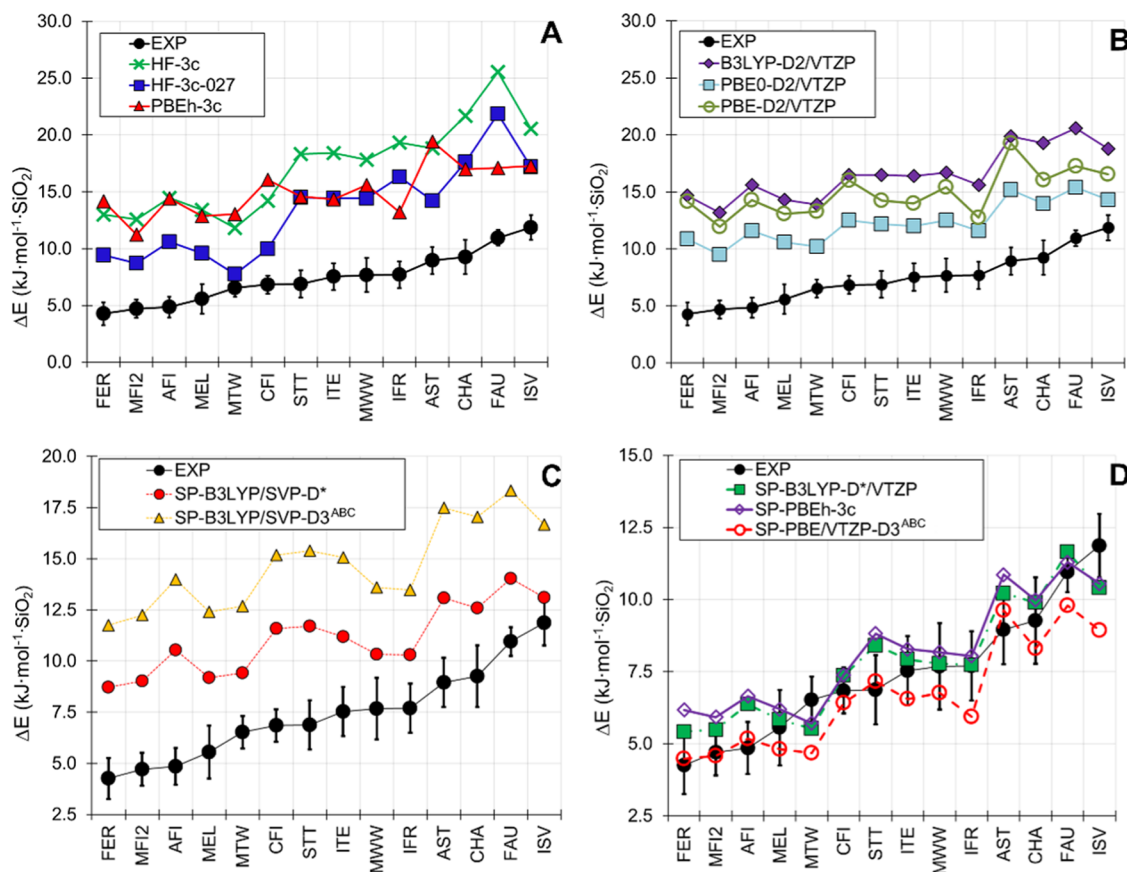
Figure 3. (A–D) Comparison between calculated and quasi-experimental energy of formation of zeolites with respect to α-quartz (see text for further details). The error bar is added to the reference data.

Table 2. Statistical Deviation (with Respect to the Quasi-Experimental Values) of the Calculated Energy of Formations of Zeolites from α-Quartz in kJ mol^{-1} per SiO$_2$ Unit^a

	ME	MAE	SD	P
HF-3c	9.8	9.8	2.4	0.9
HF-3c-027	5.9	5.9	2.5	0.8
PBEh-3c	7.6	7.6	1.6	0.7
B3LYP/VTZP-D2	9.2	9.2	1.2	0.9
PBE0/VTZP-D2	4.9	4.9	1.2	0.9
PBE/VTZP-D2	7.5	7.5	1.7	0.7
SP-B3LYP/SVP-D3^{ABC}	7.3	7.3	1.2	0.8
SP-B3LYP/SVP-D*	3.7	3.7	1.1	0.9
SP-B3LYP/VTZP-D*	0.46	0.81	0.87	0.92
SP-B3LYP/VZTP-D3^{ABC}	4.1	4.1	1.1	0.9
SP-PBE/VTZP-D3^{ABC}	−0.7	1.0	1.0	0.9
SP-PBE/VZTP-D2	−1.6	1.6	1.1	0.9
SP-PBEh-3c	0.7	1.1	1.0	0.9

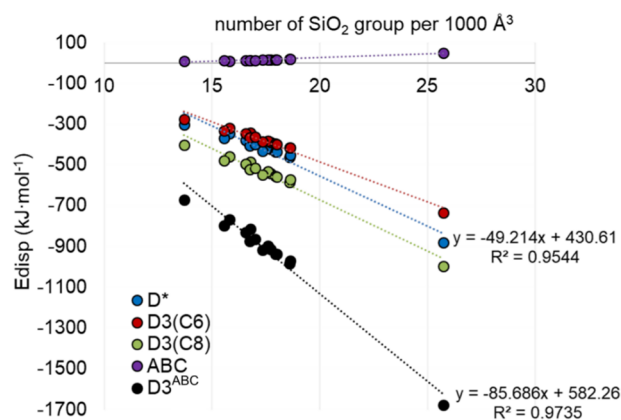^{a}P is the Pearson coefficient as defined in the Supporting Information.

Figure 4. Correlation between dispersion energy as computed with both D* and D3 corrections (to the B3LYP functional) and the density of the SiO$_2$ polymorphs.

estimation, the HF-based methods are not as good for energy evaluation, see Figure 4A. They are not accurate nor precise, with a large value of SD, e.g., 2.4/2.5 kJ mol^{-1} per SiO$_2$ unit. The compared full DFT approaches differ only for the functional type, using the same basis set (VTZP) and dispersion correction (D2). Among them, the most accurate is PBE0 with a mean absolute error (MAE) value of 4.9 kJ mol^{-1} per SiO$_2$ unit, see Figure 3B. Interestingly, all of them

have a small SD value of maximum 1.7 kJ mol^{-1} per SiO$_2$ unit (PBE method, see Table 2).

The high accuracy/cost ratio of the HF-3c-027 method for cell volume estimation suggests the use of HF-3c-027 as a substitute of DFT in the geometry optimization procedure. Relaxing the structure is the rate-determining step in these static simulations, and the use of the faster HF-3c method leads to a notable speed-up.[5] Coupling HF-3c-027 method for geometry relaxation and DFT for the energy estimation (DFT-D//HF-3c-027 recipe, hereafter labeled as SP-DFT-D) is a
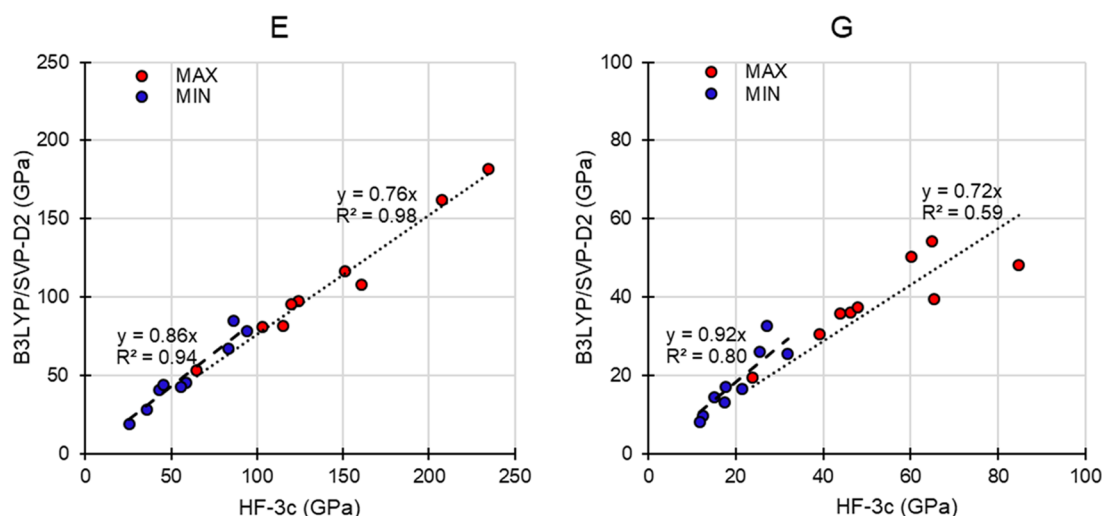
Figure 5. Minimum (black dots) and maximum (red dots) values for the Young's modulus (E) and shear modulus (G) of the zeolite set. HF-3c vs B3LYP-D2/SVP.[33] Simple linear regressions (with equation and R^2 factor) are included in the graph.

methodology that gave excellent results for computing the energetics of molecular crystals and protein models.[5,28]

Unfortunately, in terms of accuracy, the SP-B3LYP-D approach is strongly dependent on both dispersion scheme used in the energy estimation (-D) and the basis set quality, see Table 2 and Figure 3C,D. Regarding the dispersion scheme, we have tested two dispersion corrections coupled with the B3LYP functional, e.g., D* and D3^{ABC}, see Figure 3C. The SP-B3LYP/SVP-D* method is much more accurate, with a MAE of 3.7 kJ mol^{-1} per SiO_2 unit. Conversely, the SP-B3LYP/SVP-D3^{ABC} method gives a higher MAE of 7.3 kJ mol^{-1} per SiO_2 unit. The bad performance of the D3^{ABC} scheme can be explained by the overstabilization of the denser α-quartz phase with respect to the porous zeolites. For that purpose, we have plotted the dispersion energy vs density of SiO_2 group for the zeolite set (see Figure 4). The slope of the regression line is almost twice as large for D3^{ABC} with respect the D* one. Noticeable is the negligible contribution of the three-body correction. As expected, the role of the dispersion interaction is higher for denser structures, up to the maximum for α-quartz.

Within the SP-DFT-D recipe, using a larger basis set for the DFT energy estimation stabilizes the zeolite with respect to the α-quartz phase. This effect has already been seen in ref 26. This leads to results that are in very good agreement with the experiments. Indeed, for the SP-B3LYP/VTZP-D*, the calculated MAE and SD are 0.81 and 0.87 kJ mol^{-1} per SiO_2 unit, see Figure 3D. This method predicts the zeolite "quasi-experimental energy of formation" within the experimental error in most of the cases (9 out of 14). Similar level of accuracy is achieved using the PBEh-3c as well as the PBE/VTZP-D3^{ABC} methods as DFT method for the energy estimation (SP-PBEh-3c and SP-PBE/VTZP-D3^{ABC} methods), see Table 2 and Figure 3D.

In the case of the SP-PBE/VTZP-D method, the simulations corrected by the D3^{ABC} dispersion scheme give better results than those corrected by the D2 scheme (Table 2). By the analysis of the dispersion energy vs density curve, see Figure S1, we see that the slope of the regression line is similar between the D3^{ABC} scheme and the D2 one.

The accuracy of the energy of formation is very important for studying the experimental feasibility of synthesis of a given silica framework. This has been considered through the analysis of the MAE statistical function. Parallelly, we also carried out the analysis of the Pearson coefficient. It indicates the goodness of the linear correlation between experimental and theoretical data, see Table 2. In most of the cases, the theoretical methods employed have a good correlation with the experimental data. This suggests the capability of the selected method of predicting, with fair accuracy, the right stability ranking of an all-silica zeolite set.

Mechanical Stability. To tighten the comparison between different methods, we have predicted the second-order elastic properties of 9 out of 14 frameworks of the zeolite set at the HF-3c level of theory. The mechanical properties of the chosen zeolites have already been investigated in literature.[33] From the analysis of the elastic tensor, we have calculated and analyzed the Young's modulus (E) and shear modulus (G) values. These two quantities are useful for characterizing the stiffness of a material, and, therefore, they can be related to the mechanical stability of the zeolites. Due to the anisotropic nature of the crystals, E and G are directional properties, thus assuming different values depending on the direction within the crystal with respect to their evaluation. As we are only interested in checking the performance of HF-3c method with respect to the DFT reference values, we considered only the minimum and maximum values assumed by E and G for all zeolites. The reference values are computed by the B3LYP-D2/SVP method, which were taken from ref 33. The comparison is reported in Figure 5, the statistical analysis is reported in Table S5, and all explicit values are reported in Table S6.

HF-3c tends to overestimate the stiffness of the zeolites with respect to B3LYP/SVP-D2, see Figure 5, with an increment of the minimum/maximum values for E and G of $\approx 20/30\%$, see Table S5. In general, E is computed more precisely than G with an averaged SD of 11 and 20%, respectively, with respect to the DFT computed values. To correct the HF-3c values, we propose a simple scaling factor to estimate E and G at the B3LYP/SVP-D2 level starting from the HF-3c ones through a simple linear regression of HF-3c values vs B3LYP/SVP-D2 ones (see Figure 5 equations).

We have also employed the HF-3c-027 method for computing the mechanical properties. The results deviate more from the B3LYP/SVP-D2 one than the plain HF-3c. This

is not surprising, considering that the HF-3c-027 method performs badly in general in terms of energy estimation.[5] With the scaled method, the E and G values are usually higher with respect to plain HF-3c, see Figure S3.

Finally, we have calculated the E and G anisotropies, which are the difference between the maximum and the minimum values for E and G, respectively. This quantity is usually employed as a qualitative indicator of the mechanical stability of microporous crystalline materials.[33−35] The anisotropy at the B3LYP/SVP-D2 level spans from 1 to 4. Interestingly, the same range of anisotropy is computed using the HF-3c method.

CONCLUSIONS

In this work, we have reported the performance of two recently presented computational methods, e.g., HF-3c and PBEh-3c. The testing ground is the prediction of the thermodynamic and mechanical stability of all-silica zeolites. We have carried out a comparison with experiments (when available) and standard DFT simulation (also taken from literature) used as reference.

The first computational step to calculate the thermodynamic and mechanical stability of a crystalline material is the structure relaxation. An outcome of this step is the prediction of the crystal cell volume. In this regards, we have a clear indication of the excellent performance of the HF-3c method. Indeed, it outperforms PBEh-3c and standard hybrid DFT with a large basis set (from ref 26), resulting in extremely high accuracy. In details, the HF-3c-027 method computes the unit cell volumes with unsigned percentage mean error (MARE) of 1.9% with respect to experiments. The PBEh-3c method has a lower MARE of 4.4%, which is better than that of standard hybrid DFT (MARE of 5.7% at least). Interestingly, we notice an increasing accuracy in the volume prediction by increasing the percentage of the HF exchange potential within the adopted Hamiltonian. It should be stressed that due to the high cost of the calculations, we did not include any vibrational contribution, neither zero point nor thermal, on the computed volumes, which may introduce small variations in the predicted values. Nonetheless, literature data based on classical force fields developed for all-silica materials gave variations in the unit cell volumes for selected zeolites within 1%. Therefore, we think this effect will not affect the main conclusions of this work.

Regarding zeolite thermodynamic stability, we used quasi-experimental energy of formation as reference values. These data are obtained by correcting back the experimental enthalpies of formation with respect to α-quartz for the vibrational zero point and thermal energy computed at HF-3c-027 level. We found this correction to be quite constant across the set of zeolites (about 2.3 ± 0.3 kJ mol^{-1} per SiO_2 unit). In this way, we computed quasi-experimental energies of formation spanning from 4 to 12 kJ mol^{-1} per SiO_2 unit. For the HF-3c methods, we calculate a high mean unsigned error (MAE) of 5.9 kJ mol^{-1} per SiO_2 unit at least. This is not surprising, as HF-3c is known to be inaccurate for energy estimations.[5,28] Conversely, PBEh-3c does better but suffers from the relevant deviation on the unit cell volume compared to experiments.

Mixing the HF-3c method (for geometry optimization) with hybrid DFT (for single point energy calculation), namely, SP-DFT-D, is an excellent recipe to predict the thermodynamic stability of zeolites. Using the B3LYP/VTZP-D* method for energies gives a MAE value of only 0.81 kJ mol^{-1} per SiO_2 unit,

well within the experimental error for 9 out of 14 zeolites. Moreover, we noticed that B3LYP simulation corrected for dispersion with the most recent DFT-D correction, e.g., D3^{ABC} scheme, overstabilizes the dense α-quartz phase, thus destabilizing excessively the zeolites set. This effect is mitigated when the PBE functional is employed. This suggests the use of D* and D3^{ABC} schemes coupled with the B3LYP and PBE functionals, respectively, for theoretical works on pure silica zeolites.

The SP-DFT-D approach is potentially cheaper than the standard DFT. Indeed, the computationally demanding procedures, e.g., geometry optimization and vibrational frequencies estimations, are computed with the faster HF-3c method. The slower hybrid DFT (with large basis set) is used only for one single point energy calculation. The computational cost of a SCF cycle plus atomic gradient follows this order: HF-3c < B3LYP/SVP < PBEh-3c < B3LYP/VTZP. The speed-up factor of HF-3c with respect to B3LYP/VTZP is up to 1 order of magnitude with a much smaller footprint on the requested random-access memory. The speed-up can be dramatically improved by a careful reparameterization of the basis set of second-row elements in the context of solid-state application. Our group is currently working on this topic, and preliminary results indicate that the speed-up obtained for organic systems (HF-3c/(B3LYP/TZP) = 1:∼40) is attainable also for crystals of inorganic nature with properly cured basis sets.[5,28]

The calculation at HF-3c of the Young (E) and shear modulus (G) gives stiffer zeolites with respect to the B3LYP-D* prediction. The average increment on E/G values is ≈20/30%. The E and G anisotropies, which give a rough estimation of the mechanical stability of a material, are computed as the ratio between E_{max}/E_{min} and G_{max}/G_{min}. Due to errors cancellation, HF-3c agrees with B3LYP, with predicted anisotropies spanning from 1 to 4. This indicates HF-3c as a possible method to perform mechanical stability screenings of microporous materials.

In perspective, the combination of the cost-effective HF-3c method with the more accurate B3LYP/VTZP-D* one may also extend the possibility to study the adsorption of molecules in zeolite pores.[36] It can become an useful complementary tool for experimentalists for locating metal doping[37] or substitution sites in zeolites framework. In these cases, in which usually the crystal symmetry is reduced, having a fast method for computing geometry and vibrational frequencies is mandatory. The accuracy of the energy estimation, ensured by using the DFT, allows also to have reliable reaction barrier energies, as we demonstrated in conformational changes of proteins.[28] Another potential application, which will be the focus of future work, will be the study of the relative stability of different sites of protonation for Al-exchanged zeolites, which is relevant in catalysis. The PBEh-3c method confirms a reasonably good performance also of the inorganic materials. The results are in line with large basis set hybrid DFT at a fraction of their cost.

COMPUTATIONAL METHODS

We computed relaxed geometries, energies, and vibrational frequencies with a development version of the CRYSTAL14 code.[38] Conversely, zeolite mechanical properties are run with the latest release of the code, e.g., CRYSTAL17.[39] The results obtained with the development version of CRYSTAL14 can now be reproduced with CRYSTAL17.

Simulations are run employing the HF-3c[18] and PBEh-3c[22] methods, which are available in the CRYSTAL code. Along with the plain HF-3c method, we also employed a revised form of the method, namely, HF-3c-027.[5] In the HF-3c-027 approach, the dipole−quadrupole contribution of the D3 scheme is scaled by a factor of 0.27. With this refinement, HF-3c-027 gave excellent results in computing protein and molecular crystal structures, see refs 5 and 28.

Standard DFT simulations were run using the B3LYP hybrid functional,[9] corrected with a revised version of the D2 dispersion scheme, e.g., D*.[40,41] B3LYP simulations are run also with the most recent D3 scheme,[20] including the Axilrod−Teller−Muto-three-body-term (D3^{ABC}).[42,43] Also, pure GGA PBE functional has been employed, being regularly applied in plane waves based codes. The PBE functional has been coupled with the D2 dispersion scheme (scaled by a factor of 0.75),[9] and to the D3^{ABC} scheme. To estimate the volume expansion of the α-quartz, we used the quasi-harmonic approximation (QHA keyword) as implemented in the CRYSTAL17 code, using default parameters beside the parameter step and points set to 1.5 and 7, respectively, see ref 44. Due to the small cell size of the α-quartz, the QHA calculation has been carried out on a super (1 × 1 × 2) cell.

Atomic positions and cell vectors optimization adopted the analytical gradient method. The Hessian was upgraded with the Broyden−Fletcher−Goldfarb−Shanno algorithm.[45−47] We set tolerances for the convergence of the maximum allowed gradient and the maximum atomic displacement to default values. To help the convergence of the SCF, the Fock/KS matrix at a given cycle was mixed with percentage from 30% up to 50% of the one of the previous cycle.[44] The recently introduced direct inversion of the iterative subspace extrapolator technique has been employed to speed up the SCF convergence.[48,49] Details on the tolerance values controlling the Coulomb and exchange series in periodic systems[44] and the shrink factor used in the calculations are reported in details in the Supporting Information. Regarding the shrinking factor, a minimum shrinking factor of 2,2 was employed up to 6,6 depending on the system. The zeolite mechanical properties were calculated employing the default setup of the CRYSTAL17 code, besides the NUMDERIV parameter, which is set to 5.[44] For the vibrational frequency calculations, the mass-weighted force-constant matrix was computed at the Γ point by numerical derivative of the analytic nuclear gradients. A value of 0.003 Å was chosen as the displacement of each atomic coordinate. The IR intensity of each normal mode of vibration was computed using the Berry phase approach.[50] Tolerance (Hartree) on the energy convergence is set to

- 10^{-7} for single point energy calculations and geometry optimizations
- to 10^{-8} in mechanical property calculations (as default)
- to 10^{-11} in frequency calculations.

B3LYP calculations were carried out using molecular all-electron Gaussian basis sets. A split valence basis with polarized functions (SVP) set of 8-411G(d) was chosen for O atoms and 88-31G(d) for Si atoms.[51] Also, a more extended VTZP basis set from Ahlrichs et al.,[52] also employed in the work of Román-Román et al.,[26] has been adopted here for running B3LYP simulations. The HF-3c method is implemented and parameterized only for the MINIX[18] basis set, which is a STO-3G-like quality basis set for O, whereas polarization functions are added for the Si atom. The PBEh-3c method has the def2-mSVP basis set, which is a 535-1111G(d) and DZP set for Si and O, respectively.

To compute the quasi-experimental energy of formation, $\Delta E_{q\text{-}exp}$, we applied the formula

$$\Delta E_{q\text{-}exp} = \Delta H_{exp}(298) - \Delta E(ZPE) - \Delta E(298)$$

in which $\Delta E(ZPE)$ and $\Delta E(298)$ are the zero point energy and the thermal corrections, respectively, to the experimental enthalpy of formation $\Delta H_{exp}(298)$. The graphical visualization and structural manipulation of structures was performed with MOLDRAW version 2.0.[53] Images were rendered with VDM.[54] Analysis of the elastic tensor was carried out with the ELATE online tool.[55]

■ ASSOCIATED CONTENT

⑤ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03135.

Shrinking factor used in all calculations (Table S1); TOLINTEG values used in the calculations; statistical functions and basis sets details (Table S2); zeolite-optimized volume (Table S3); calculated and experimental energy of formation (Table S4); correlation between dispersion energy and the density of the SiO_2 polymorphs (for the PBE functional) (Figure S1); IR spectra of the zeolite set (Figure S2); statistical analysis of the calculated mechanical properties (Table S5); minimum and maximum values for the Young's modulus and shear modulus (Table S6); E_{min}, E_{max}, G_{min}, and G_{max} correlation (Figure S3) (PDF)

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The authors declare no competing financial interest.

■ DEDICATION

This work is dedicated to the memory of our dear friend Claudio M. Zicovich-Wilson.

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