



Cite this: *Phys. Chem. Chem. Phys.*,
2025, 27, 4187

Prediction of NMR parameters and geometry in ^{133}Cs -containing compounds using density functional theory†

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The need to immobilize low-level nuclear waste, in particular ^{137}Cs -bearing waste, has led to a growing interest in geopolymer-based waste matrices, in addition to optimization attempts of cement matrix compositions for this specific application. Although the overall phase composition and structure of these matrices are well characterized, the binding sites of Cs in these materials have not been clearly identified. Recent studies have suggested that combining the sensitivity of solid-state nuclear magnetic resonance (SSNMR) to the local atomic structure with other structural techniques provides insights into the mode of Cs binding and release. Density functional theory (DFT) can provide the connection between spectroscopic parameters and geometric properties. However, the reliability of DFT results strongly relies on the choice of a suitable exchange–correlation functional, which for ^{133}Cs , the NMR surrogate for such studies, is not well-established. In this work we benchmark various functionals against their performance in predicting the geometry of various simple Cs compounds, their NMR quadrupolar coupling constants, and their chemical shift values, while prioritizing the ability to incorporate dispersion interactions and maintaining low computational cost. We examined Cs salts, Cs oxides, perovskites, caged materials, a borate glass and a cesium fluoroscandate. While no single functional performs equally well for all parameters, the results show rev-vdW-DF2 and PBEsol+D3 to be leading candidates for these systems, in particular with respect to geometry and chemical shifts, which are of high importance for Cs-immobilization matrices.

Received 3rd September 2024,
Accepted 28th January 2025

DOI: 10.1039/d4cp03451a

rsc.li/pccp

Introduction

Cesium is an alkali metal whose ionic form plays a key role in various materials and applications, including chemical catalysis,¹ purification of biological macromolecules,² and optoelectronic devices.³ Radioisotopes of Cs, specifically ^{137}Cs , a β -emitter with a half life time of ~ 30 years, are found in radioactive waste streams. The long term immobilization of Cs-bearing radioactive waste is a challenging task due to the high solubility of Cs ions in aqueous media. Whereas vitrification is the method of choice for high-level nuclear waste,^{4,5} cementitious matrices are usually used for low-level and intermediate-level waste immobilization due to their low cost and ease of preparation, combined with good mechanical properties and durability under irradiation. However, cesium is not efficiently immobilized by the alkaline environment

afforded by cement. Geopolymers have been proposed as an alternative for Cs-bearing low-level nuclear waste due to their ability to specifically bind Cs ions.⁶ Examples from recent years are the many studies regarding immobilization of incineration ashes from the Fukushima region, which have a high content of radioactive ^{134}Cs and ^{137}Cs following the nuclear accident in 2011. Alkaline activation of the ashes leads to the formation of geopolymeric wasteforms^{7–9} consisting of various crystalline and amorphous phases. The ultimate Cs immobilizing matrix should be characterized by high Cs binding, and consequently minimal leaching to the environment under relevant environmental conditions. High-resolution structural characterization of Cs-bearing matrices, clarifying properties such as the binding site(s) geometry, the binding phase where several phases coexist, and the equilibrium distribution between competing sites, can contribute to the rational design of improved immobilization matrices.

Parameters provided by solid-state NMR (SSNMR), such as chemical shift, dipolar coupling, and quadrupolar coupling, are sensitive to the local geometry of the studied nuclei, including its binding atoms, bond lengths and angles, and its non-covalent interactions with the environment. Thus, they contain

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4cp03451a>



a wealth of local geometric and electronic structure information. However, only few examples show how ^{133}Cs SSNMR can be utilized to characterize Cs binding sites in nuclear waste matrices.^{4,10–17}

In general, there is no simple, straightforward method to directly infer structural properties from the NMR parameters, unless the dipolar interaction, which is proportional to the inverse cube of the distance, is directly measured. First-principles calculations are known to bridge the gap between spectroscopy and structure, thus allowing to utilize the information content of SSNMR to its fullest. Density functional theory (DFT) has been in vast use in the physics and chemistry communities for decades due to its ability to predict diverse properties such as ground state structure, excitation energies, spectroscopic properties, reaction energies and more, for molecules and solids, with high accuracy and at a relatively modest computational cost. Specifically, the use of DFT calculations side by side with NMR measurements has become widespread since the introduction of the GIPAW (Gauge Including Projector Augmented Wave) method,^{18–20} which provides the ability to compute NMR tensors in solid systems with all-electron accuracy. Although DFT has been helpful in the structural characterization of zeolites,^{21,22} ^{133}Cs has not been extensively studied using DFT-GIPAW. Relevant examples of the combination of ^{133}Cs SSNMR and DFT are the study of Cs adsorption on Montmorillonite clay,¹² and their use to study Cs-containing perovskites²³ and cryptands.²⁴

Prior to the use of DFT-GIPAW for probing Cs binding in complex systems such as cements and geopolymers, which are often a conglomerate of several crystalline and non-crystalline phases, it is instructive to screen the suitability of different DFT functionals to correctly predict ^{133}Cs NMR parameters using simpler, well characterized Cs-containing systems. Cs-halides (CsF, CsCl, CsBr, and CsI) are the obvious place to start. Experimentally, it is well known that under ambient temperature and pressure, CsF crystallizes in the B1 phase (Fig. 1(a)), forming the so called NaCl or rock-salt structure, as most alkali halides do. However, CsCl, CsBr, and CsI crystallize in the B2 phase (Fig. 1(b)), being the only alkali halides known to crystallize in the so-called CsCl structure under these conditions²⁵ (the discussion omits Fr and At, about which no data is available).²⁶ The reason for this difference is dispersion interactions which favor the phase with the shorter distances

between ions of the same kind, that is, the CsCl phase. These interactions depend on the ion polarizability, and are therefore more substantial in the mentioned systems consisting of heavy ions.^{27,28} Van der Waals forces make only a minor contribution to the total lattice energy of an ionic lattice (1–5% of the lattice energy), but they are the factor determining the phase in this case.²⁸ Zhang *et al.*²⁹ have shown that despite the simplicity of cesium halide structures, the popular Perdew–Burke–Ernzerhof (PBE)³⁰ functional, commonly used for the prediction of NMR parameters for ^{133}Cs ^{12,23} and other nuclei,^{31–34} fails to predict the correct phase for CsCl. The same also occurs when using other GGA-type functionals such as the solid-state optimized PBEsol,²⁹ PW91 and revPBE,³⁵ as well as for various *meta*-GGA type functionals (MS0, MS1, MS2, TPSS and rTPSS).³⁵ A plausible explanation is that pure DFT functionals do not include terms describing dispersion forces.^{29,36} Pure DFT functionals are semilocal, meaning that the energy density at any point depends only on properties at that point. Consequently, these functionals are by definition unable to model dispersion, which is an interaction between instantaneous dipoles at two different sites. Indeed, the correct CsCl structure is obtained using calculation schemes incorporating dispersion.^{29,37}

Dispersive interactions can be introduced into DFT by various approaches.³⁶ A common approach is the addition of asymptotic dispersion corrections to the energy obtained by a standard DFT calculation, in the manner of an interatomic potential.^{38–45} Notable examples of dispersion corrections are the Grimme schemes DFT+D,³⁸ DFT+D2³⁹ and DFT+D3;⁴⁶ Tkatchenko-Scheffler (TS) dispersion correction⁴⁰ and the subsequent many-body dispersion (MBD) correction,⁴⁷ and exchange-hole dipole-moment model (XDM).^{48–50} Asymptotic dispersion corrections can attain good accuracy at a relatively low computational cost, and can be applied in conjunction with various, well-tested functionals. Another approach is the development of explicitly non-local density functionals,^{51–58} whereby the energy depends on the density and its gradient at two points in space simultaneously. Notable examples of non-local functionals are vdW-DF,⁵³ vdW-DF2,⁵⁶ vdW-DF3,⁵⁹ and rVV10.^{54,57} Additional methods include dispersion-correcting potentials,^{60–63} and parameterized exchange–correlation functionals.^{64–66} Finally, *meta*-GGA functionals^{67,68} can incorporate short-range, but not long-range, dispersion interactions through their dependence on the kinetic energy.

For Cs halides, forcing the right phase upon the popular PBE functional yields a good prediction of the chemical shift,⁶⁹ but does not solve the problem of the accurate geometry prediction. It is currently unknown which functional can correctly capture both the geometry and the NMR parameters of Cs-compounds, ranging from Cs halides to Cs-bearing zeolites.

This work aims to identify the most suitable DFT scheme for the prediction of the correct geometry and NMR parameters of various Cs-containing systems. First, we screen various functionals for their ability to predict the correct phase in Cs halides. We then compare their performance in predicting the crystal unit cell volume, chemical shift and quadrupolar coupling constants in Cs halides, Cs oxyanion compounds, and

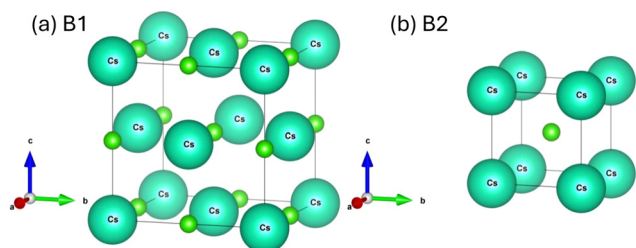


Fig. 1 (a) B1 (NaCl) phase vs. (b) B2 (CsCl) phase unit cells.²⁵ The large spheres represent the metal, whereas the small ones represent the halide. At room temperature, only CsF adopts the B1 phase.



Cs-containing perovskites. Keeping in mind our interest in more computationally-demanding Cs-bearing materials, we have restricted this study to schemes of a reasonable computational cost. Differences in the performance and accuracy of various functionals, as well as their performance compared with experimental results available in the literature, are discussed, and recommendations for functional selection for the prediction of ^{133}Cs NMR parameters are proposed.

Computational methods

DFT calculations were carried out using the Quantum Espresso 7.1^{70,71} software package, which uses the gauge-including projector augmented waves (GIPAW) method for computing magnetic resonance properties of crystalline structures. We used scalar relativistic PAW PBE or PBEsol pseudopotentials,⁷² downloaded from the Quantum Espresso website. Spin-orbit coupling (SOC) effects on the geometry were found to be sufficiently small to be neglected at this stage and were not further considered (see ESI,† Table S13). The plane wave cutoff energies for eighteen cesium-containing systems, determined by convergence tests, are listed in Table S1 in the ESI.† The kinetic energy cutoff was four times that of the wave function. Monkhorst-Pack grids were used to sample the Brillouin zone (see Table S1, ESI† for their dimensions), and the initial structures were taken to be the reported crystal structures (Table S2, ESI†).

Various functionals and dispersion corrections were used for the calculations of geometry and NMR parameters. PBE,³⁰ known to fail in predicting the correct phase in cesium halides, is used as a reference, being a very common functional. Other GGA-type functionals examined here are revPBE,⁷³ a one-parameter modification of PBE; its further modification rPBE,⁷⁴ which performs well for the calculation of NMR parameters in solids containing elements of the third and fourth periods;^{75,76} PBEsol,⁷⁷ tailored to solids; and B86bPBE,^{30,78} the recommended functional to be paired with XDM for solid state calculations.⁴⁴ These five semilocal functionals are used as base functionals in conjunction with three dispersion corrections – DFT-D2,³⁹ DFT-D3,⁴⁶ and XDM.^{50,79} PBE+MBD was not used as it is known to fail to converge for many cesium halides, and neither was PBE+TS which is known to yield the correct phase but provide incorrect lattice constants.⁸⁰ Non-local functionals considered are rVV10,⁵⁸ vdW-DF1,⁵³ vdW-DF2,⁵⁶ vdW-DF3,⁵⁹ vdW-DF-C6,⁸¹ rev-vdW-DF2 (also called vdW-DF2-B86R).⁸²

Asymptotic dispersion corrections (such as D2, D3, and XDM) are implemented post-self-consistently, meaning they do not affect the electron density. Therefore, for a given geometric structure, the NMR properties, which strongly depend on the electronic structure, will be unaffected by these corrections. In contrast, nonlocal functionals are formulated self-consistently, directly influencing the electron density. However, all dispersion corrections of any type can indirectly affect any molecular property *via* their effect on the geometric structure. For this reason, we found it instructive to compare the NMR

parameters obtained by different functionals using either the experimental (crystallographic) geometry or the DFT-optimized geometry, allowing us to distinguish between geometry-mediated effects and electronic-structure-mediated effects. In the cases where structural relaxation was implemented, both the lattice constants and the atomic positions were optimized using the BFGS algorithm, until the residual forces acting on each atom were below 1.0×10^{-3} Ry a.u.⁻¹.

Results and discussions

Cesium halide polymorphs

Pure DFT functionals are known to fail in the prediction of the ground state structure of heavy Cs halides, owing to the absence of dispersion in the energy calculation. Therefore, the first criterion for DFT scheme screening was the ability to correctly predict the ground state phase, which is B1 for CsF and B2 for heavier Cs halides. Unfortunately, the comparison to experiment is only qualitative, as the experimental values of the energy gap between Cs halides polymorphs are unavailable.

The results confirm that semilocal functionals erroneously assign the B1 phase to all Cs halides (Fig. 2(a)). Interestingly, the slope of the energy gap curve is the same for all five GGA-type functionals tested here, with the exception of PBEsol for the CsF–CsCl segment. The addition of an asymptotic dispersion correction leads to the correct phase prediction in most, yet not all, combinations of base functionals (PBE, rPBE, revPBE, PBEsol, B86bPBE) and dispersion corrections (D2, D3, and XDM) tested here. The D2 correction (Fig. 2(b)) using the default parameters leads to a non-physical trend where the energy gap is non-monotonous *versus* the halide size and was therefore not further used. Using Zhang's parameterization for Cs $\left(C_6^{\text{Cs}} = 57.74 \frac{\text{J nm}^6}{\text{mol}}, R_0^{\text{Cs}} = 1.776 \text{ \AA} \right)$ ²⁹ rectifies this. Using Schurko's D2* reparameterization of the damping function⁸³ ($d = 3.25$ instead of the default 20), originally implemented using rPBE, on its own leads to a nearly flat curve and a wrong phase in CsF. Using Zhang's parameters together with D2* does not settle the phase issue and does not reproduce the trend with respect to the halide size. We note that D2* was parametrized using the EFG tensors of three elements, and should in principle be transferrable to all elements. However, it was designed to provide a good fit of the EFG, not necessarily of the phase stability, and was trained on small organic molecules, very different from the inorganic salt structures studied here.

The D3 and XDM corrections (Fig. 2(c)) lead in most cases tested here to the correct phase, although the trend is violated for PBE+D3, PBEsol+D3, and B86bPBE+XDM (the curves go slightly up from CsBr to CsI). A similar behavior was described for PBE+D3 with Li halides.⁸⁴ The energetic gap between the phases is larger for PBE (or PBEsol)+D2 than for PBE (or PBEsol)+D3. This can be explained by the fact that D2 describes dispersion using only two-body attractive interactions, whereas D3 also incorporates local environment effects and three-body repulsive interactions.⁸⁵



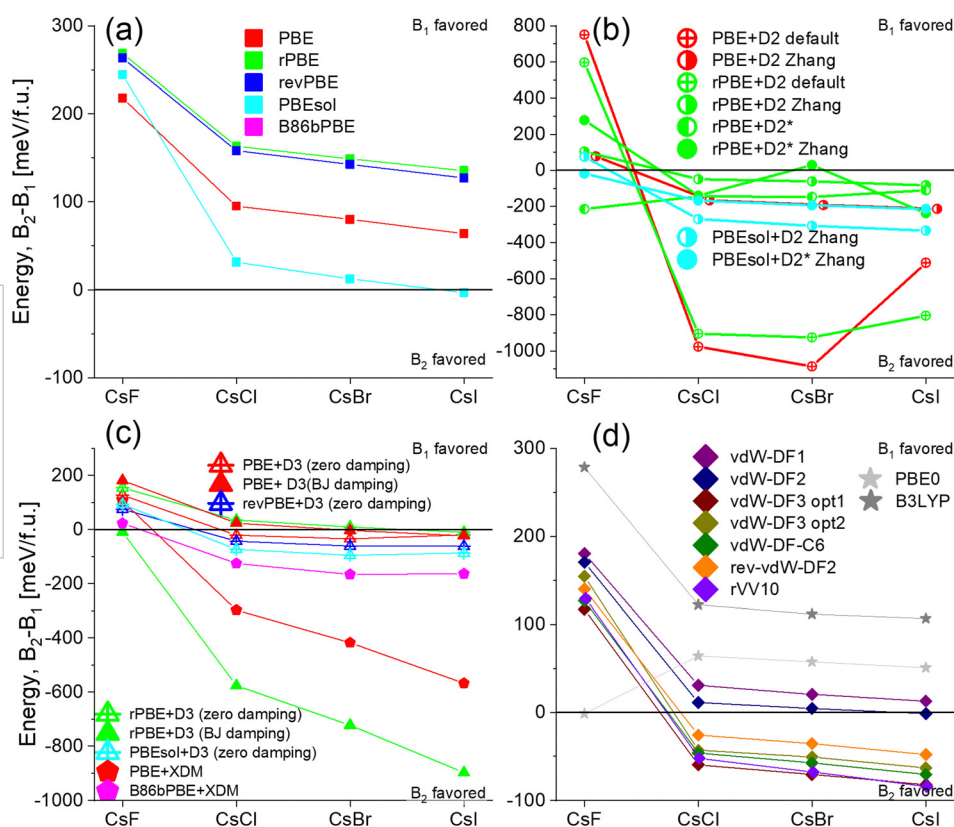


Fig. 2 Relative stability of Cs halide phases for various functionals: (a) semilocal functionals (■); (b) semilocal functionals with DFT-D2 dispersion correction (○; the symbol filling indicates the parametrization used); (c) semilocal functionals with DFT-D3 dispersion correction (△, the filling indicates the type of damping function used) or XDM (●) dispersion correction; (d) non-local (◆) and hybrid (★) functionals.

All vdW-DF functionals tested (Fig. 2(d)) yield curves of the same slope. Most of them yield the correct phase, as does rVV10. The hybrid functionals tested here do not capture the correct phase.

The reliable structure prediction of Cs halides is challenging, since the energy gap between competing phases, caused by the typically weak dispersion forces,²⁸ is small, and is therefore very sensitive to errors arising in various approximations of the exchange–correlation energy. The energy gaps predicted here are similar to those calculated by Pyper (0.078 eV f.u.⁻¹),⁸⁶ Aguado (0.14 eV f.u.⁻¹),⁸⁷ and Zhang (0.16 eV f.u.⁻¹).²⁹ As shown by others,²⁹ GGA and hybrid functionals fail to predict the correct phase of Cs halides. We therefore chose to proceed with non-local and dispersion-corrected semilocal functionals.

Unit cell volume

In the next step of this study the ability of different functionals to predict the unit cell volume of Cs compounds was tested. The panel of Cs-compounds was expanded to include additional systems, namely four Cs oxyanion salts and three CsGeX₃ perovskites in addition to the four Cs halides studied thus far. Fig. 3 features unit-cell volumes obtained from X-ray diffraction (literature values) and calculated unit cell volumes obtained

using various DFT schemes, along with the mean error (ME) for each functional. We note that the DFT results refer to 0 K, while the experimental structures were determined at or around room temperature.

Most schemes give a reasonable prediction of the unit cell volume, and correctly capture the trend among different compounds. Quantitatively, however, there are differences between various schemes. As expected, PBE overestimates the unit-cell volume. Adding a dispersion correction to PBE results, as expected, in a contraction of the calculated unit cell, to an extent that depends on the type of dispersion correction used. D2 is superior to XDM and D3 in this context, with XDM leading to an underestimation of the cell volume. The functionals revPBE+D3 and B86bPBE+XDM are outperformed even by uncorrected PBE. This is in contrast to the good performance of B86bPBE-XDM in predicting the lattice constant of the entire series of alkali halides.⁸⁸ This may be related to the fact that unlike the former study,⁸⁸ the current work includes compounds containing polyatomic anions. Good performance is also displayed by the non-local functionals, as well as by rPBE+D2* Zhang parametrization and PBEsol+D3. The tested non-local functionals are the best performers in this task, as manifested by both their small mean error and their small standard deviation values.



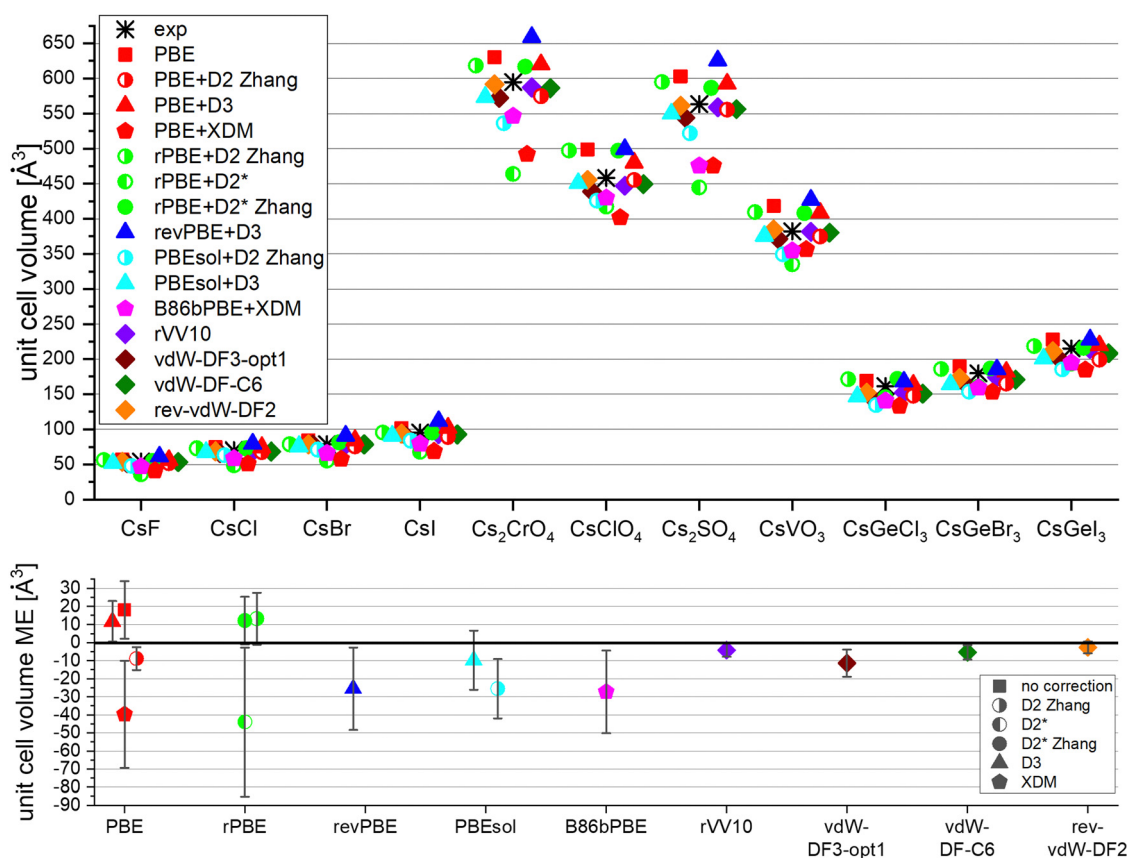


Fig. 3 Unit-cell volume of various Cs-containing compounds as found experimentally by X-ray crystallography (asterisk) or by calculation using various DFT schemes. Some of the points are slightly horizontally shifted to avoid overlap. See Table S2 (ESI†) for references of the experimental data. The bottom figure show the mean error (ME) of each functional. The error bars represent the standard deviation (1 SD above and below the mean). The mean relative error (MRE) and the coordinates root-mean-square-error (RMSE) are found in Fig. S1 (ESI†).

^{133}Cs NMR parameters: The quadrupolar coupling constant

The calculation of the ^{133}Cs quadrupolar coupling constant C_q , using GIPAW and the same DFT schemes, is shown in Fig. 4. A great difference is noticeable between different compounds: some are very sensitive to the calculation scheme (e.g. CsClO_4 , CsVO_3), whereas some are not (e.g. CsGeX_3 , Cs_2CrO_4 site 2, Cs_2SO_4 site 1). This observation highlights the importance of screening a large sample of materials before choosing which calculation scheme to use.

PBE, though not accounting for dispersion and not providing an accurate unit cell volume (Fig. 3), provides a very good prediction of the C_q parameter, slightly outperformed only by PBE+D3 and rPBE+D2* Zhang. Adding D2 or XDM to PBE leads to an overestimation of $|C_q|$, although PBE+D2 yields good geometry (Fig. 3). The other combinations of a GGA functional with an asymptotic dispersion correction are not better in terms of absolute error, but adding Grimme's D3 correction improves the relative error. All four non-local functionals yield similar results and are all inferior to PBE and to PBE+D3, although their unit cell volume prediction was better (Fig. 3).

Interestingly, when using the experimental geometry without geometry optimization (empty squares), all schemes tested

here provide nearly identical results. It is not surprising that the semilocal functionals provide results similar to each other, as do the non-local functionals. However, it is not obvious that these two different families of functionals provide results similar to each other, despite the fact that dispersion is inherent in the non-local functionals, while this is not the case in the corrected ones. We therefore conclude that the main effect determining the accuracy of C_q here is the geometric structure, not the difference in the functional itself. This is in agreement with other studies.⁸⁹ However, remarkably, the functionals excelling at geometry prediction (e.g. rVV10, rev-vdW-DF2) do not excel at C_q prediction, showing that the structure most similar to the experimental one is not necessarily the one leading to the best C_q , at least for the type of Cs compounds studied here. Moreover, geometry optimization often results in a higher deviation in the C_q predicted value from that of the experimental value, with the exception being uncorrected PBE, PBE+D3, and rPBE+D2* Zhang parameterization. We note that the small sample of materials used here, owing to the scarcity of experimental ^{133}Cs NMR results in the literature, results in large standard deviation values. Still, a fairly linear correlation is maintained between



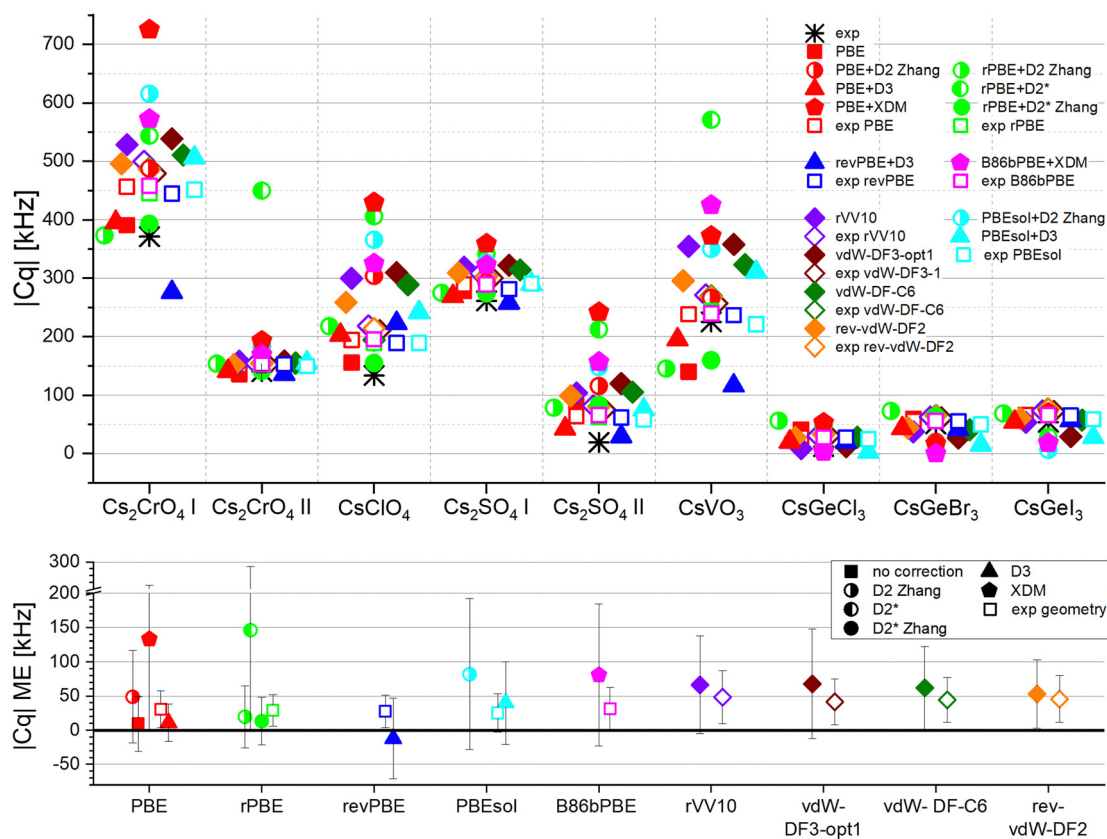


Fig. 4 Quadrupolar coupling constant C_q of various Cs compounds. The black asterisks correspond to the experimental values (Table S3, ESI[†]), whereas the colored symbols correspond to computational results (Tables S4–S6, ESI[†]). Solid symbols represent calculations where the geometry was optimized, whereas open symbols correspond to calculations employing the experimental (XRD) geometry. The bottom plot shows the mean error in C_q . Additional error metrics are given in Fig. S1 (ESI[†]). The error bars represent the standard deviation.

calculated and experimental C_q values (Fig. S2 and Table S7, ESI[†]).

An important aspect in the analysis of ^{133}Cs , is that in many materials of interest the value of its quadrupolar coupling constant is small, and its experimental measurement is therefore difficult, also due to its high spin ($S = 7/2$). The chemical shift, which has a relatively broad ppm range, becomes the more informative ^{133}Cs NMR observable. We therefore turn to calculations of ^{133}Cs shifts.

^{133}Cs NMR parameters: Chemical shifts

We have used DFT calculations to predict the ^{133}Cs chemical shielding tensor. To convert the absolute shielding to the chemical shift, we plotted in Fig. 5(a) the calculated isotropic shieldings *versus* the experimental isotropic shifts. Experimental values have been obtained from various literature sources, as shown and referenced in Table S8 (ESI[†]), as well as experiments performed in our lab. A literature review revealed that for the simple Cs salts we analyzed, different reference compounds have been used and occasionally spectral referencing was not clearly stated. ^{133}Cs chemical shifts are known to be concentration dependent,⁹⁰ and the use of a solution containing Cs^+ as an external reference must be done with

care, in particular when using hygroscopic compounds such as CsNO_3 . The commonly cited manuscript by Haase⁹¹ contains data from experiments performed on static samples and at a low field (2.1T), and reports that a solution of 0.5 m CsCl resonates at +6.1 ppm with respect to infinite dilution, and that solid CsCl is at 228.1 ppm. A later study by Mooibroek⁹² reports solid CsCl to be +223.2 ppm with respect to 0.5 m CsCl, and this value is more commonly used in the literature, although various studies also use a 0.5 M or 1 M CsCl solution as the reference value of 0 ppm. Our experimental data, measured under 5 kHz magic-angle spinning at a field of 14.1T, shown in Fig. S4 (ESI[†]), allowed us to reconcile the seemingly contradicting literature results, setting a uniform reference scale. We used solid CsCl as a reference at +223.2 ppm, obtained that a 1 M CsCl solution has a chemical shift of 5.0 ppm, and from several solutions of CsCl the infinite dilution chemical shift value is projected to -6.1 ppm, in agreement with Haase and the correction by Mooibroek for solid samples. All experimental values obtained from the literature were therefore re-referenced using the corrected scale. To demonstrate the usefulness of using solid CsCl as a reference, we also show in Fig. S4 (ESI[†]) that its chemical shift is independent of temperature, whereas for 0.1 M CsNO_3 in D_2O (IUPAC recommendation), a shift of 1.9 ppm is observed over 15 °C.



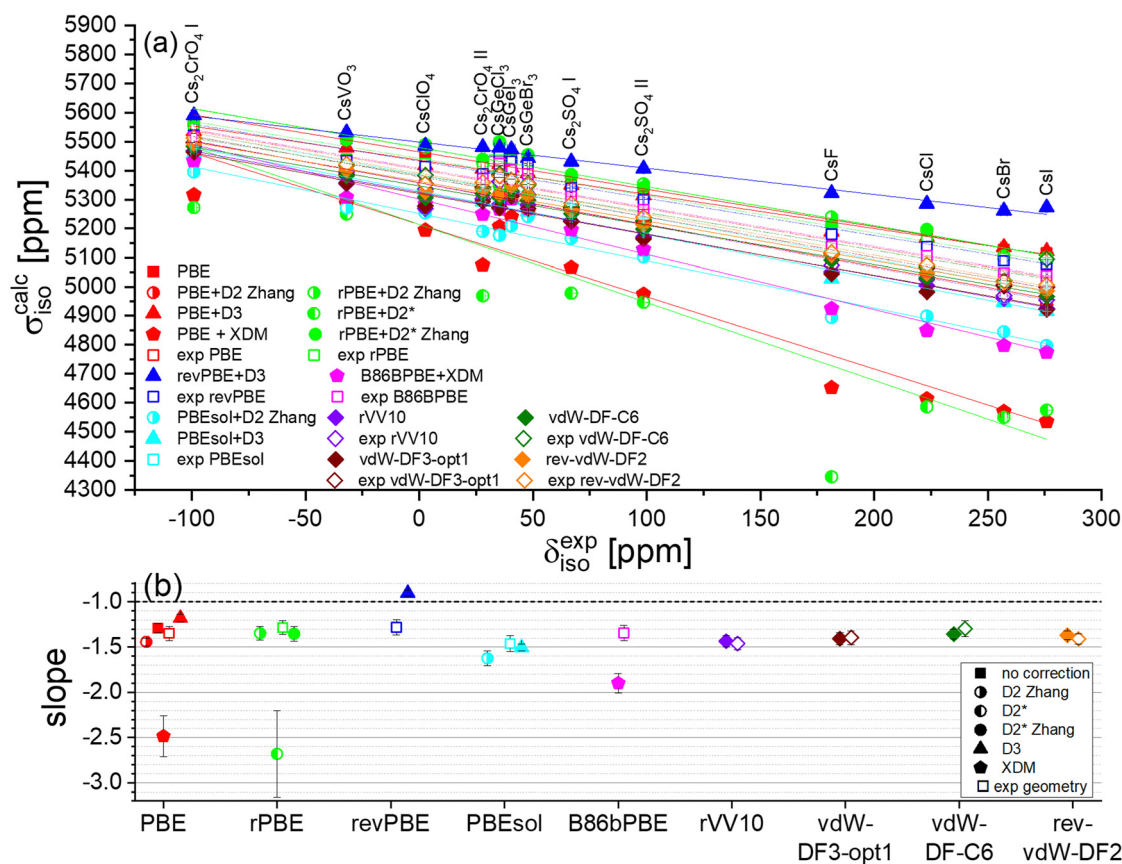


Fig. 5 (a) Linearization plots of the isotropic shielding of various schemes and (b) their corresponding slopes. The error bars of the slopes represent standard deviations. δ_{iso} are averaged experimental results collected from the literature (re-referenced) and from our own measurements (Table S8 and Fig. S4, ESI†).

The correlations between the re-referenced experimental chemical shifts and calculated chemical shielding, presented in Fig. 5(a), reveal that most calculation schemes are well fitted by linear curves, with the exception being rPBE+D2*. However, the slopes differ from the ideal value of -1 (Fig. 5). The greatest deviations from the ideal slope are those of XDM corrected functionals and of rPBE+D2*, the latter being greatly improved by adding Zhang's parametrization along with that of D2*. The slopes closest to -1 are those of revPBE+D3 (-0.90 ± 0.03) and PBE+D3 (-1.18 ± 0.04). Most other functionals feature slopes in the range $[-1.45, -1.2]$, the differences between most functionals being insignificant, even when comparing, for example, between uncorrected semilocal functionals using the experimental geometry and non-local ones including geometry optimization.

We used the fitted correlations to convert the calculated chemical shieldings to shifts. The results, plotted in Fig. 6, show that all functionals capture the general trend in the chemical shifts of different systems. However, quantitative accuracy differs between different schemes. When using the experimental geometry, the shift is nearly independent of functional, as reported in other studies,⁹³ and as we observed in the prediction of C_q . Geometry optimization improves the

accuracy for most schemes, in contrast to the case of C_q calculation. While for experimental geometry the mean absolute error (MAE) of δ_{iso} values is mostly between 15–20 ppm (empty symbols), the best accuracy after optimization is achieved by PBEsol+D3 (MAE = 6.2 ppm), rev-vdW-DF2 (8.9), PBE+D2 (9.7), revPBE+D3 (10.4), PBE+D3 (10.5), rVV10 (10.8), and vdW-DF-C6 (10.9). These MAE's amount to 3% of the total shift span (372 ppm). Interestingly, it has been shown that PBE+D3 does not perform well in the calculation of ^{13}C chemical shift in zeolites,⁹³ whereas PBEsol+D3 is usually not used for chemical shift calculations.

Again, the limited availability of experimental ^{133}Cs NMR results manifests itself in broad error margins, precluding a definite choice of the best-performing functional. However, the functionals displaying a small mean absolute error also tend to display a lower standard deviation compared to the others, supporting their identification as good performers. Another comment regarding the variability of the average error, is that this variability is small for the unit cell volume (Fig. 3), but large for the NMR parameters (Fig. 4 and 6), although the sample size is nearly the same for both (not identically the same due to two of the systems containing two Cs-sites each). This suggests that for many functionals, the performance in geometry



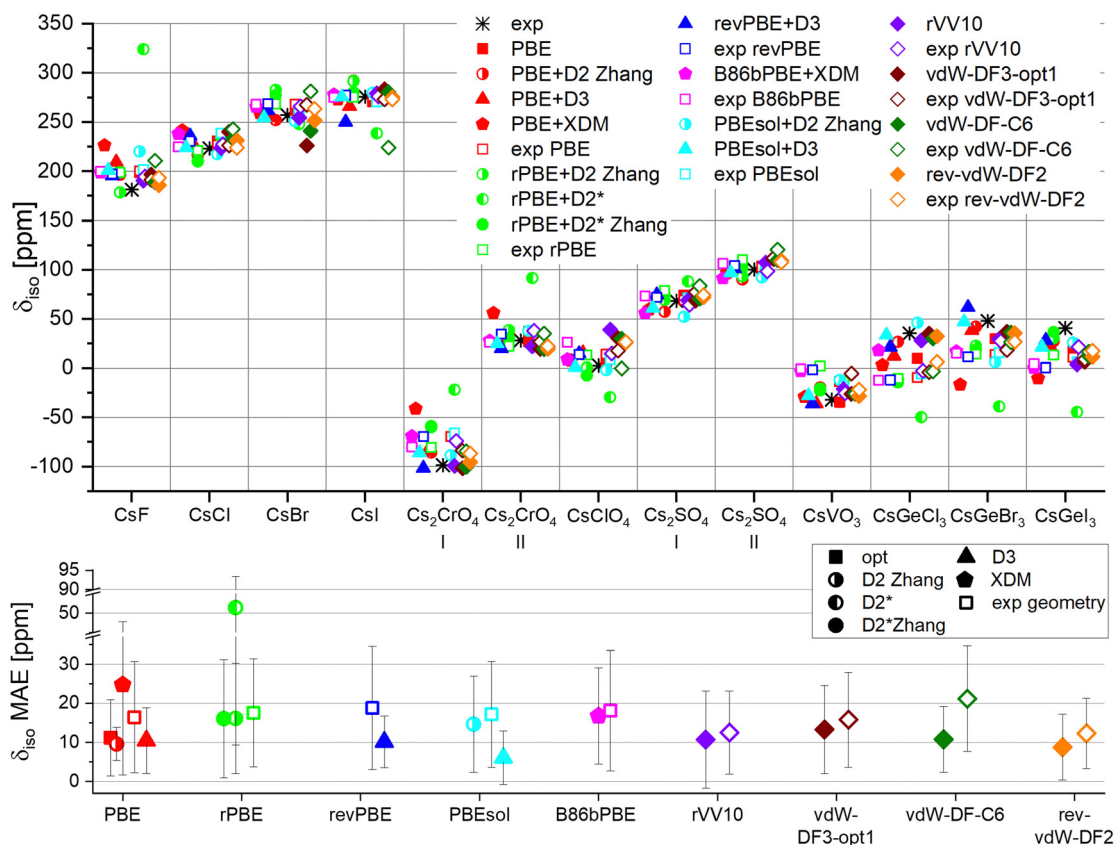


Fig. 6 Computational and experimental values of the isotropic chemical shifts for various Cs compounds. Experimental values (Table S8, ESI[†]) were partly measured by us (spectra shown on Fig. S4, ESI[†]) and partly by others. The bottom plot shows the mean absolute error in δ_{iso} . Error bars represent standard deviation. An additional error metric is found in Fig. S1 (ESI[†]). The calculated shifts, after linearization, are explicitly given in Tables S9–S12 (ESI[†]).

optimization is quite the same for different materials, but the performance of GIPAW for NMR parameters calculation is more sensitive to the system.

To distinguish between a systematic tendency rather than a random error in the estimation of the chemical shift, we also show the mean signed error in Fig. S1 (ESI[†]). For all tested functionals, the MSE is practically zero, indicating a random error.

When zooming in on a more subtle trend, that of the isotropic chemical shift *versus* the halide size (Fig. 7), and observing the apparently best functionals for the chemical shift

prediction, it can be seen that revPBE+D3 fails to predict the trend in CsI, whereas rev-vdW-DF2 and PBEsol+D3, which were successful for the Cs halides, fail in CsGeX₃ (note that the parabolic shape, where the maximum is at Br, is kept). Only PBE+D3 qualitatively captures the halide trends in both series.

Chemical shift anisotropy (CSA) values have also been calculated for the various materials, and are shown in Fig. S5 in the ESI[†].

Overall performance of functionals – Cs halides, oxyanions, perovskites

The mean errors of all functionals (including geometry optimization) for the unit cell volume, isotropic shift, and quadrupolar coupling constant are summarized in Fig. 8.

PBE characteristically overestimates the unit cell volume, while providing good (yet not the best) NMR parameters. Adding the D2 correction leads to an underestimation of the cell volume while marginally improving the accuracy of the chemical shift. Adding the D3 correction to PBE leads to very good overall performance, among the best in each of the three observables. XDM correction to PBE or B86bPBE, leads to a major underestimation of the cell volume, as well as to poor chemical shift prediction. rPBE+D2, using Zhang's parametrization for Cs, provides good accuracy in the geometry, but not

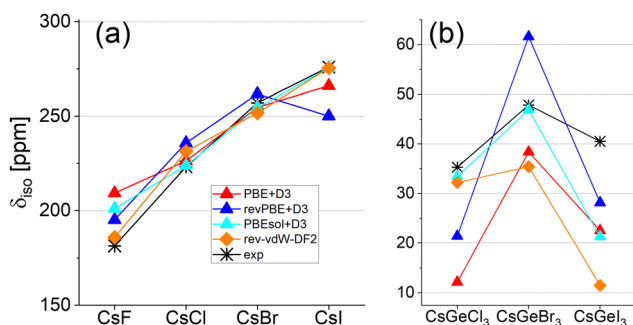


Fig. 7 Isotropic chemical shifts for (a) Cs halides and (b) Perovskites (cesium germanium halides).



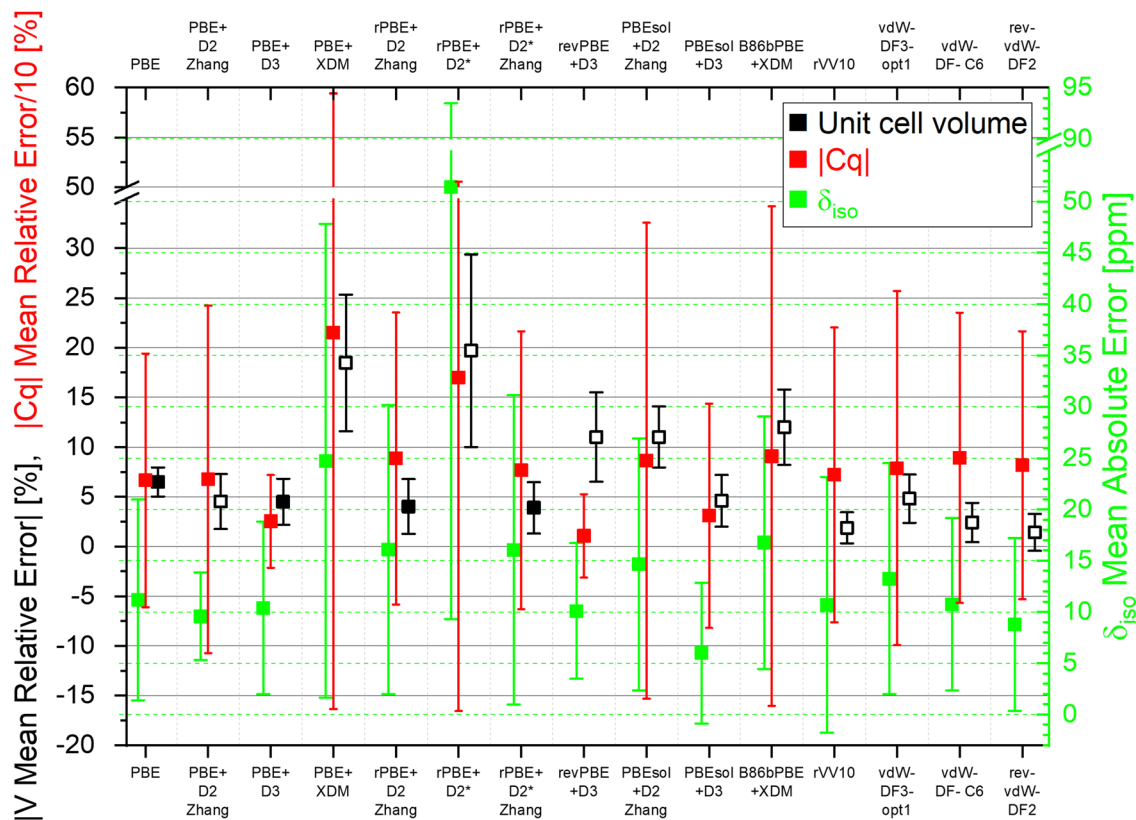


Fig. 8 MRE of the unit cell volumes (black, empty squares are for negative values), MAE of the isotropic chemical shifts (green), and MRE of the quadrupolar coupling constants (red) for all schemes. Symbols represent mean values; error bars represent standard deviation.

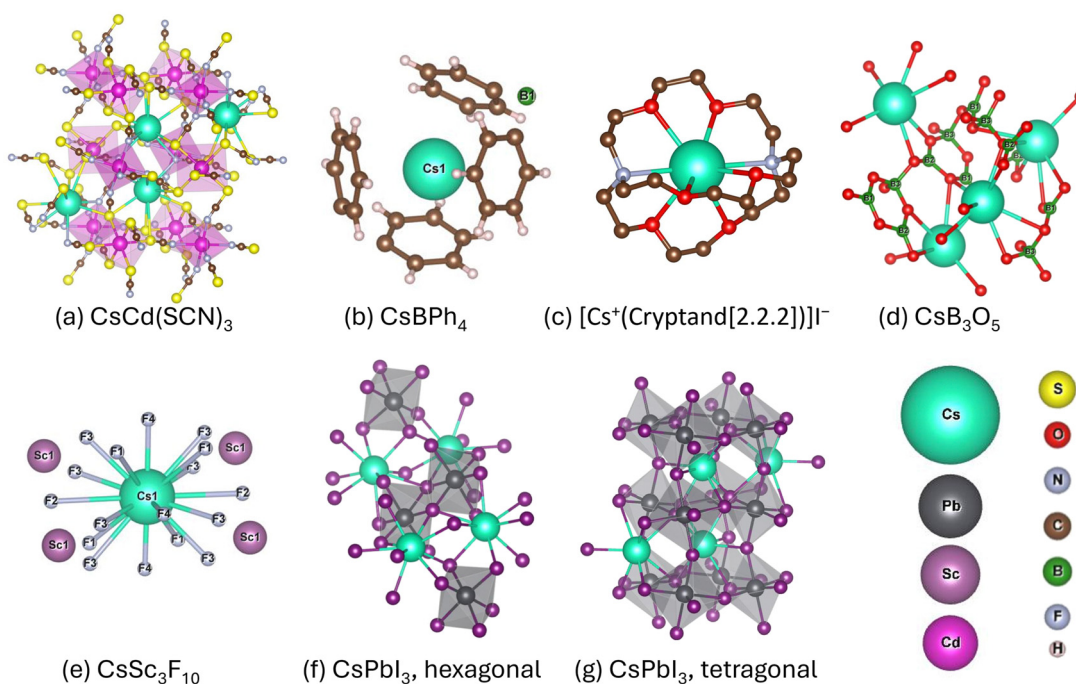


Fig. 9 Structures of (a) $\text{CsCd}(\text{SCN})_3$,⁹⁶ (b) CsBPh_4 ,⁹⁷ (c) $[\text{Cs}^+(\text{Cryptand}[2.2.2])]\text{I}^-$,⁹⁴ (d) CsB_3O_5 ,⁹⁸ (e) $\text{CsSc}_3\text{F}_{10}$,⁹⁹ (f) hexagonal CsPbI_3 ,¹⁰⁰ (g) tetragonal CsPbI_3 .¹⁰¹



in the NMR parameters. Schurko's D2* parametrization has a marginal effect only. Interestingly, PBEsol+D2 fails in the geometry, but performs well for the NMR parameters (but with larger than typical standard deviations). Likewise, revPBE+D3 fails in the geometry, but surprisingly excels in C_q prediction, while performing well for the shift. PBEsol+D3 performs very well, among the best, for the volume and the quadrupolar coupling, and excels in chemical shift. Its overall performance is among the best.

rVV10, vdW-DF-C6 and rev-vdW-DF2 excel at the unit cell prediction, while performing among the best in the chemical shift, and provide reasonably good quadrupolar coupling constants. vdW-DF3-opt1 is slightly inferior to them.

To sum up, this panel shows PBE+D3, PBEsol+D3, rVV10, vdW-DF-C6 and rev-vdW-DF2 to display good overall performance in predicting the geometry and NMR parameters of Cs salts, oxyanions and perovskites.

Extension to additional systems

To examine whether the results obtained using Cs salts, oxyanions and perovskites are transferrable to different Cs-containing

systems, we applied the best performing functionals to very different systems, the structures of which are shown in Fig. 9.⁹⁴ These systems differ from those in the set used in the previous section in several ways. CsCd(SCN)₃ (Fig. 9(a)) is again a perovskite, but it contains a heavier element, Cd; in CsBPh₄ (9b) Cs interacts with induced dipoles in the aromatic rings, unlike the ionic systems studied above; in [2.2.2] cryptand (9c) Cs interacts with electronegative atoms (O, N) in the altogether neutral complex *via* ion-dipole interactions, forming a stable coordination complex encapsulating the metal in a spheroidal cavity, somewhat analogously to Cs binding to zeolites, although with shorter Cs-O distances; CsB₃O₅ (9d) is a glassy system; in CsSc₃F₁₀ (9e) the coordination number of Cs is uncharacteristically high (18); CsPbI₃ (9f-g) is challenging due to the presence of the heavy Pb atom, in addition to Cs. Hence, we also compared in Fig. S6 (ESI[†]) our calculations to those obtained including SOC showing that improvement is system dependent.⁹⁵

Here again we examine the prediction of unit cell volume, the quadrupolar coupling constant, and the isotropic chemical shift. The results are shown in Fig. 10.

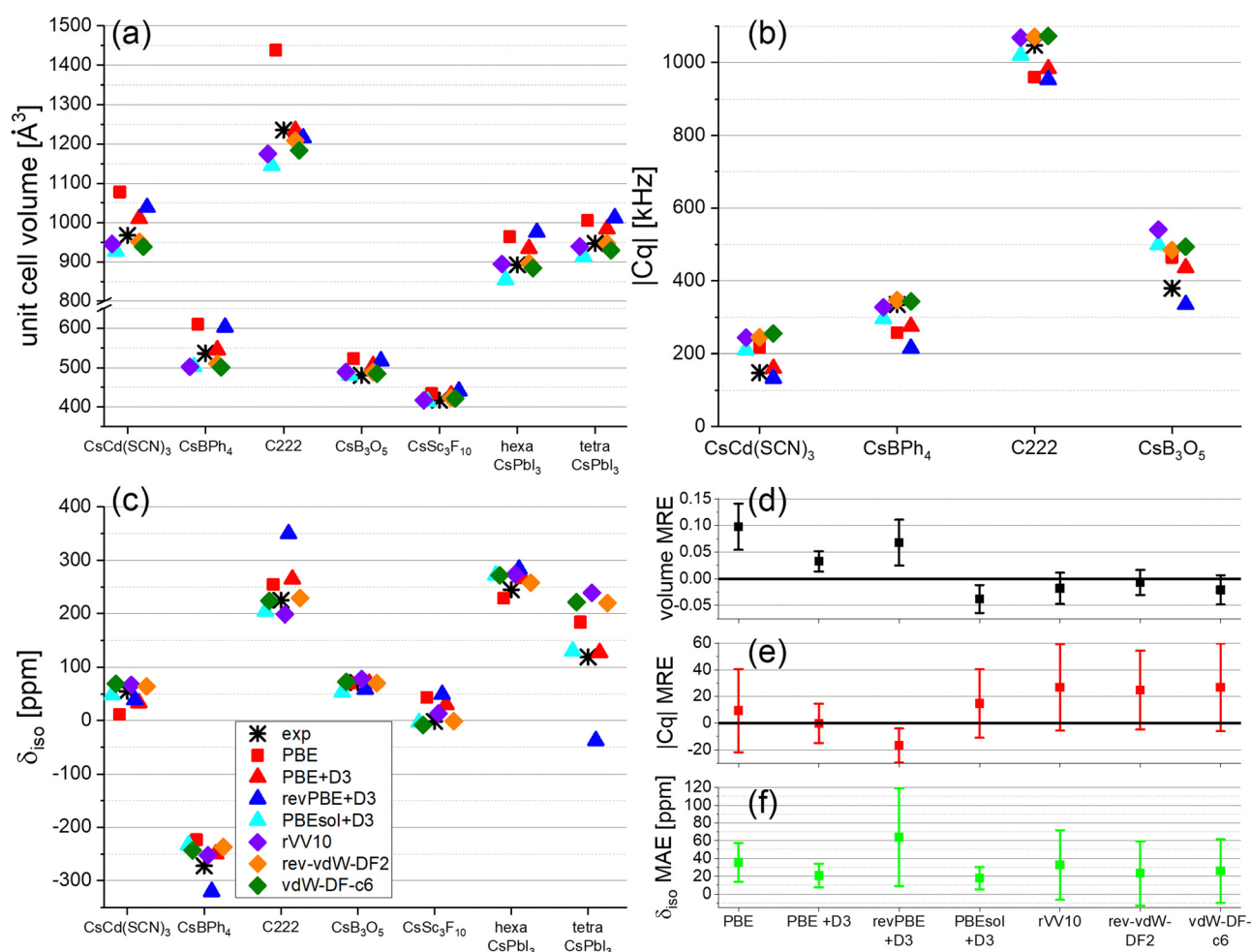


Fig. 10 (a) Unit cell volume, (b) C_q , (c) δ_{iso} and (d)–(f) error analysis. Symbols represent mean values; error bars represent standard deviation. See ESI,[†] Table S8 for references of experimental values.



As shown in Fig. 10, here again the PBE functional overestimates the unit cell volume, while performing reasonably well (but not the best) in C_q . Its chemical shift performance is similar to that of most other functionals considered at this stage. PBE+D3 excels in the geometry, while being on-par with others in chemical shift, in line with the previous results (Fig. 4 and 6). RevPBE+D3 shows the largest error in chemical shift, despite a relatively good geometry prediction, unlike the previous results. PBEsol+D3, which was the best performer in chemical shift for the simple systems, followed closely by rev-vdW-DF2, is again comparable with the latter in all three observables. All non-local functionals tested here excel at geometry prediction. Rev-vdW-DF2⁸² has previously been shown to successfully predict the structural, mechanical, cohesive and vibrational properties of both weakly and strongly bound solids,¹⁰² as well as the interlayer binding energy of multilayered solids¹⁰³ and the adsorption energy of adsorbed molecules.^{104,105} It is however not yet widely used for chemical shift prediction,¹⁰⁶ and we are unaware of C_q calculations using this functional. We are also unaware of studies using PBEsol+D3 for the calculation of NMR parameters.

To conclude, switching from small systems to more complicated and diverse compounds, PBEsol+D3 and rev-vdW-DF2 maintain their overall good performance and relative advantage. While we cannot determine if this conclusion holds for other materials due to the relatively small (20) set of distinct Cs sites studied here, these functionals appear to be a promising choice for the determination of Cs geometry and NMR parameters, in particular chemical shifts that are more useful for distinguishing between the chemical environments of Cs.

Summary & conclusions

A series of DFT functionals were screened for their performance and accuracy in the prediction of the geometry, quadrupolar coupling constants, and chemical shifts of cesium-133 in Cs-based halides, oxyanions and perovskites. The functionals chosen were those considering dispersive interactions, in order to faithfully predict the phase of Cs halides, while keeping a low computational cost. The best performing functionals, chosen mainly based on their performance with respect to geometry and isotropic chemical shift predictions, were then tested on seven additional materials, which exhibit chemical environments, bonding and coordination that are different than the above-mentioned inorganic compounds, including interactions of the Cs cation with polar groups resembling to some extent Cs caged in zeolites. Overall, we examined 20 different Cs sites from 18 different compounds. While no single functional performs best for all parameters (geometry, chemical shift, quadrupolar coupling), the results suggest that two of the functionals tested, rev-vdW-DF2 and PBEsol+D3, maintained their advantage in predicting both geometry and isotropic shifts in these seven additional diverse materials.

Further work should be dedicated to the implementation of these functionals to the more challenging systems such as

zeolites or geopolymers, used for the sequestration and immobilization of radioactive Cs species. More advanced (and computationally more expensive) *meta*-GGA and various hybrid functionals, possibly in combination with dispersion corrections may also be considered for these structurally complex systems.

As this work was the first stage of functional screening, it did not incorporate SOC, whose computational cost would have limited the number of tested systems and functionals. Further studies will have to consider the contribution of SOC to the accuracy and precision in predicting geometry and NMR parameters.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was partially funded by the Pazy Foundation grant ID 701-2025. We thank Orr Simon Lusky for preparing the CsNO₃ solution.

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