A Hybrid Density Functional Theory Benchmark Study on Lithium Manganese Oxides

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(Dated: January 30, 2020)

The lithium manganese oxide spinel Li$_x$Mn$_2$O$_4$, with $0 \leq x \leq 2$, is an important example for cathode materials in lithium ion batteries. However, an accurate description of Li$_x$Mn$_2$O$_4$ by first-principles methods like density functional theory is far from trivial due to its complex electronic structure, with a variety of energetically close electronic and magnetic states. It was found that the local density approximation as well as the generalized gradient approximation (GGA) are unable to describe Li$_x$Mn$_2$O$_4$ correctly. Here, we report an extensive benchmark for different Li$_x$Mn$_2$O$_4$ systems using the hybrid functionals PBE0 and HSE06, as well as the recently introduced local hybrid functional PBE0r. We find that all of these functionals yield energetic, structural, electronic, and magnetic properties in good agreement with experimental data. The notable benefit of the PBE0r functional, which relies on on-site Hartree-Fock exchange only, is a much reduced computational effort that is comparable to GGA functionals. Furthermore, the Hartree-Fock mixing factors in PBE0r are smaller than in PBE0, which improves the results for (lithium) manganese oxides. The investigation of Li$_x$Mn$_2$O$_4$ shows that two Mn oxidation states, +III and +IV, coexist. The Mn$^{III}$ ions are in the high-spin state and the corresponding MnO$_6$ octahedra are Jahn-Teller distorted. The ratio between Mn$^{III}$ and Mn$^{IV}$ and thus the electronic structure changes with the Li content while no major structural changes occur in the range from $x = 0$ to 1. This work demonstrates that the PBE0r functional provides an equally accurate and efficient description of the investigated Li$_x$Mn$_2$O$_4$ systems.

I. INTRODUCTION

Today, a world without lithium ion batteries is hard to imagine because they are essential for the energy supply of almost all portable electronic devices from mobile phones to laptop computers. The lithium manganese oxide spinel Li$_x$Mn$_2$O$_4$, an intercalation compound with Li contents $0 \leq x \leq 2$, is a prominent example for cathode materials in lithium ion batteries,[1] which offers advantages such as low costs and non-toxicity.[2]

The Li content can be varied over a wide range of $0 \leq x \leq 2$ using, for example, electrochemical (de)intercalation.[5] At temperatures above $\sim 290$ K, for compositions $0 \leq x \leq 1$ the crystal exhibits a cubic spinel structure with the space group Fd$\overline{3}$m in which Li occupies the tetrahedral 8a sites and Mn the octahedral 16d sites (FIG. 1). The MnO$_6$ octahedra share one half of their edges with other MnO$_6$ octahedra. Each of their corners is shared with one LiO$_3$ tetrahedron in the case of LiMn$_2$O$_4$. The MnO$_6$ octahedra build a superstructure of corner-sharing (MnO$_6$)$_4$ tetrahedra. Complete delithiation results in the formation of $\lambda$-MnO$_2$ exhibiting the same manganese oxide host lattice, while all tetrahedral sites are unoccupied. Thus, no major internal structural changes occur when reducing the Li contents from $x = 1$ to $x = 0$, while the lattice constant is approximately linearly decreasing. The varying content of Li ions is balanced by changes in the oxidation states of the Mn ions to maintain overall charge neutrality. Consequently, in LiMn$_2$O$_4$, one half of the Mn ions is in the high-spin (hs) Mn$^{III}$ state ($e_g^3 \lambda_g^1$) while the other half is in the oxidation state Mn$^{IV}$ ($e_g^{1} \lambda_g^{3}$).[2] The lithium-free $\lambda$-MnO$_2$ contains exclusively Mn$^{IV}$ ions. The hs-Mn$^{III}$ ions lead to Jahn-Teller (JT) distorted
MnO$_6$ octahedra. Therefore, the cubic crystal structure can be understood as a disordered arrangement of Mn$^{III}$ and Mn$^{IV}$, in which the JT distortions are thermally averaged in all spatial directions. Below $\sim$290 K, an increasing ordering of the Mn ions and the alignment of the distorted octahedra results in a transformation of the spinel structure to an orthorhombic phase with space group Fddd. At very low temperatures, an antiferromagnetic long-range order as well as spin-glass behavior were observed.

For $x > 1$, a phase transition takes place to a tetragonal spinel structure with space group I$_4$1/amd. This transition is caused by the increasing number of Mn$^{III}$ ions and the associated JT distorted MnO$_6$ octahedra upon lithiation. A miscibility gap exists between the cubic ($x = 1$) and tetragonal ($x = 2$) spinel structure. If the average Li content is higher than $x = 1$, the tetragonal phase with $x = 2$ will form and both phases coexist in the range 1 < $x$ < 2.

Detailed insights into the structure of Li$_x$Mn$_2$O$_4$ have been gained in various experiments, e.g. X-ray diffraction, transmission electron microscopy and atom probe tomography. Theoretical studies are able to provide complementary information, for example, about the underlying atomistic processes of the phase transitions or about the Li diffusion pathways. However, the underlying electronic structure of Li$_x$Mn$_2$O$_4$ is very complex due to the large number of energetically close electronic and magnetic states. Therefore, a theoretical treatment using density functional theory (DFT) is far from trivial. Previous studies could show that the local density approximation (LDA) as well as the generalized gradient approximation (GGA) do not yield a qualitatively correct electronic structure, since all Mn ions in LiMn$_2$O$_4$ are found to be in an averaged oxidation state of 3.5. Further, in contrast to experiment no band gap exists. Consequently, GGA+U or hybrid functionals are required to correctly obtain distinct Mn$^{III}$ and Mn$^{IV}$ ions as well as a qualitatively correct band gap, which is about 1.2 eV in experiment.

Manganese is known for its wide range of possible oxidation states and complex magnetic structures of its compounds. Experimental studies could show that even elemental $\alpha$-Mn exhibits a non-collinear antiferromagnetic structure. The Mn$^{II}$ ions in MnO are arranged in a way that the antiferromagnetic order is present in all three cubic directions. The magnetic structure of the Mn$^{III}$ ions in $\alpha$-Mn$_2$O$_3$ was investigated by a combined GGA+U and neutron diffraction study. The outcome is a complex non-collinear antiferromagnetic order. In $\beta$-MnO$_2$, the Mn$^{IV}$ ions crystallize in an antiferromagnetic structure with helically ordered magnetic moments.

In this study, we investigate the accuracy of the well-established PBE0[33, 34] and HSE06[35, 36] functionals as well as the recently developed local hybrid functional PBE0r[38] for these structures and a variety of other systems containing lithium, manganese, and oxygen. The benchmarked properties include formation energies, structural properties, and the density of states. Furthermore, the magnetic order and the intercalation potential of Li$_x$Mn$_2$O$_4$ are determined. Additionally, the D3 method[39] is evaluated for these systems as a possible approximate correction to overcome limitations in the description of van der Waals interactions in current.
hybrid functionals.

The main focus of our work is on the Li$_2$Mn$_2$O$_4$ spinel structure. Therefore, our benchmark set includes spinels with varying Li contents, specifically the X-ray diffraction structures of $\alpha$-Mn$_2$O$_4$ (at room temperature),$^{[22]}$ Li$_5$Mn$_2$O$_4$ (at 293 K),$^{[23]}$ LiMn$_2$O$_4$ (at 330 K),$^{[3]}$ and Li$_2$Mn$_2$O$_4$ (at room temperature)$^{[24]}$ (FIG. 2 (a)-(d)). Moreover, several related systems, which were thoroughly investigated theoretically and experimentally before, were chosen to benchmark the exchange-correlation functionals. They comprise the X-ray diffraction structures of Li (at 78 K),$^{[25]}$ Li$_2$O,$^{[26]}$ Li$_2$O,$^{[27]}$ $\alpha$-Mn,$^{[27]}$ Mn$_3$O$_4,$$^{[28]}$ Mn$_3$O$_4,$$^{[29]}$ $\alpha$-Mn$_2$O$_3,$$^{30}$ $\beta$-Mn$_2$O$_3$ (neutron diffraction),$^{31}$ and orthorhombic LiMn$_2$O$_4,$$^{32}$ (FIG. 2 (e)-(m)). These structures, which refer to room temperature unless stated differently, cover both common Li oxidation states of 0 and +I and the Mn oxidation states 0, +II, +III, and +IV. Furthermore, the molecules H$_2$, O$_2$, and H$_2$O as well as the ice polymorph I$_h$ (neutron diffraction) at 100 K$^{[33]}$ (FIG. 2 (n)) are part of the benchmark set.

II. METHODS

While Kohn-Sham DFT is in principle exact, approximate exchange-correlation functionals $E_{xc}$ need to be employed. In recent decades, a hierarchy of functionals was proposed, which can have a notable impact on the quality of the obtained results.$^{[41,42]}$ In this work, we will address the performance of modern hybrid functionals, which currently represent the state-of-the-art, using the examples PBE0, HSE06, and PBE0r. PBE0$^{[25,33]}$ is based on the PBE$^{[44]}$ GGA functional, but 25% of the PBE exchange $E_{xc}^{\text{PBE}}$ are replaced by exact Hartree-Fock (HF) exchange $E_{xc}^{\text{HF}}$ resulting in

$$E_{xc}^{\text{PBE0}} = E_{xc}^{\text{PBE}} + \frac{1}{4} (E_{xc}^{\text{HF}} - E_{xc}^{\text{PBE}}) . \quad (1)$$

The calculation of the HF exchange increases the computational costs drastically due to the long-range nature of the Coulomb interaction. Replacing the Coulomb interaction in the exchange by a screened interaction reduces the number of integrals to be evaluated, and it recovers the subtle balance of exchange and correlation for electrons at large distances. In the HSE06 functional$^{35,37}$ this is realized by a screened Coulomb potential,

$$\frac{1}{r} = \frac{1 - \text{erf}(\omega r)}{r} + \frac{\text{erf}(\omega r)}{r} , \quad (2)$$

i.e. the Coulomb potential is separated into a short range and a long range part. The separation range is determined by the screening parameter, $\omega = 0.11 a_0$, which was empirically obtained by calibration to experimental properties.$^{37}$ $a_0$ is the Bohr radius. Consequently, the HF exchange is only calculated for the short-range part (superscript s) but not for the long-range part (superscript l), which reduces the computational cost substantially for extended systems,

$$E_{xc}^{\text{HSE06}} = 0.25 E_{xc}^{\text{HF},s} + 0.75 E_{xc}^{\text{PBE},s} + E_{xc}^{\text{PBE},l} + E_{xc}^{\text{PBE}} . \quad (3)$$

The correlation part $E_{xc}^{\text{PBE}}$ is not affected by the screened Coulomb potential. For a screening parameter $\omega = 0$ the functional is equal to PBE0. For $\omega = \infty$ the functional is identical to PBE.

The recently published PBE0r functional$^{38}$ is a local hybrid exchange-correlation functional which is also derived from PBE0. The Kohn-Sham orbitals are mapped onto a minimal basis of localized atom-centered tight-binding orbitals. The tight-binding orbitals are used to calculate the on-site HF exchange terms including the exchange interaction between core and valence electrons. All other exchange contributions, i.e. those with tight-binding orbitals centered on different atoms, are neglected. Hence, PBE0r can be regarded as range-separated hybrid functional where the cutoff of the exchange interaction is defined by the localized tight-binding orbitals. The PBE0r exchange-correlation functional $E_{xc}^{\text{PBE0r}}$ is then given by

$$E_{xc}^{\text{PBE0r}} = E_{xc}^{\text{PBE}} + \sum_{n=1}^{N} a_n (E_{xc,n}^{\text{HF},s} - E_{xc,n}^{\text{PBE},s}) . \quad (4)$$

Since the inclusion of HF exchange is restricted to the on-site terms, $E_{xc,n}^{\text{HF},s}$, only the corresponding PBE exchange terms, $E_{xc,n}^{\text{PBE},s}$, are subtracted in order to avoid double counting. The HF mixing factor $a_n$ of the $N$ atoms can vary for the chemical elements in a given system. The mixing factors are empirically determined using known experimental and theoretical data as reference. This approximate treatment of HF exchange compared to PBE0 is reasonable in strongly correlated systems like (lithium) manganese oxides, where the electrons are localized which is associated with the dominance of screened Coulomb potentials.$^{35}$ Therefore, the non-local exchange interactions are effectively screened and the long-range exchange interactions are small. However, due to the large number of terms their calculation would account for most of the computational costs. Thus, the restriction to on-site terms reduces the computational costs significantly and the introduced error is small for materials with localized electrons such as transition metal oxides. For the description of strong covalent bonds however, additional off-site HF exchange terms may have to be included.

III. COMPUTATIONAL DETAILS

The PBE0r calculations were performed using the Car-Parrinello Projector Augmented-Wave (CP-PAW) code (version from 28th September 2016) which applies the projector augmented-wave (PAW) method$^{46}$ for electronic structure calculations. The augmentation of the
PAW method included the 1s orbital of H, the 2s and 2p orbitals of Li, the 2s, 2p, and 3d orbitals of O, and the 3s, 3p, 3d, 4s, and 4p orbitals of Mn. In the case of Mn, besides the 4s and 3d orbitals also the 3s and 3p orbitals were treated as valence electrons, because these semi-core states are required to describe the electronic structure of Mn in the systems of the benchmark set properly. The matching radii for the construction of the auxiliary partial waves in units of the covalent radii were set to 0.7 for all orbitals. The covalent radii were set to 0.32 Å for H, 1.23 Å for Li, 0.73 Å for O, and 1.17 Å for Mn. The auxiliary wave functions were constructed as node-less partial waves.\cite{47} The tight-binding orbitals include the 1s orbital of H, the 2s orbital of Li, the 2s and 2p orbitals of O, and the 3s, 3p, 3d, and 4s orbitals of Mn. The mixing factors \( a_m \) for the HF exchange were adjusted to minimize the errors of the formation energies and band gaps of the benchmark set using experimental reference data, which are given and referenced in the following chapter. The obtained \( a_m \) values are 0.07 for H, 0.07 for Li, 0.05 for O, and 0.09 for Mn. The complete settings for each element are given in the Supporting Information (SI). As the non-collinear treatment of the spins would increase the computational effort for the benchmark systems significantly, the approximation of collinear spin-polarization was applied. The plane wave cutoff was 25 \( E_H \) (Hartree) for the auxiliary wave functions and 100 \( E_H \) for the auxiliary densities. With these settings, the obtained formation energies deviate less than 0.01 eV per atom from the complete basis set limit. The \( \Gamma \)-centered \( k \)-point grid was set to 2\( \times \)2\( \times \)2 for the LiMn\( _2 \)O\( _4 \) unit cell, and for the other systems \( k \)-point grids of a comparable \( k \)-point density were chosen. For metallic systems, the improved tetrahedron method was used.\cite{18} This ensures a convergence level of about 0.001 eV per atom for energies differences. Molecular systems were placed in a large periodic cell with lattice vectors (0 11.5 11.5)\( ^T \) Å, (12 0 12)\( ^T \) Å, and (12.5 12.5 0)\( ^T \) Å using only the \( \Gamma \)-point. The long-ranged electrostatic interactions were decoupled from the periodic images for the molecules.\cite{49} The cell size was converged so that no artificial interactions between periodic images are taken into account for molecular systems. Wave function and geometry optimizations were performed using the Car-Parrinello ab-initio molecular dynamics method\cite{50} with a friction term which quenches the system to the ground state. This enabled efficient optimizations of the atomic positions in the unit cell. The computational costs of geometry optimizations increased only by roughly a factor of 2 compared to single-point calculations depending on the initial structure. For metallic systems, the Mermin functional\cite{51} was applied to treat variable occupations of the one-electron energy eigenstates. The total energy was minimized up to a numerical convergence of \( 10^{-5} E_H \) for the given settings. PBE\( _{PAW} \) calculations were performed with the CP-PAW code as well using the same settings with the exception that all HF mixing factors were set to zero. The PBE, HSE06, and PBE0 calculations were performed using the Fritz-Haber-Institute ab initio molecular simulations (FHI-aims) package (version 160328.3)\cite{52} which is an all-electron electronic structure code with numeric atom-centered basis functions. Again, a collinear treatment of the spin-polarization was applied. The default light basis set of FHI-aims was used which achieves a finite basis set error of less than 0.04 eV per atom for energy differences like formation energies. A \( \Gamma \)-centered \( k \)-point grid was used for periodic systems. The density of the \( k \)-point grid was the same as in the CP-PAW calculations. The error of the finite \( k \)-point grid is less than 0.001 eV per atom for energy differences unless metallic systems are present, then the error can be up to 0.04 eV per atom. Molecular systems were calculated in a non-periodic environment which saved computational resources while full numerical consistency of the settings with periodic calculations was maintained. Geometry optimizations were performed using the Broyden-Fletcher-Goldfarb-Shanno algorithm\cite{53,54} up to a numerical convergence of 0.001 eV of the system’s total energy whereby the used forces provide an accuracy of \( 2 \cdot 10^{-4} \) eV/Å. An exception were the \( \alpha \)-Mn calculations where the total energy and forces were only converged up to 0.01 eV and \( 2 \cdot 10^{-3} \) eV/Å, respectively. The total energies themselves were converged in every iteration of the geometry optimizations in a self-consistent field procedure to a numerical accuracy of \( 10^{-5} \) eV. For metallic systems, the zero-broadening corrected energies were used. Further details of the FHI-aims calculations are given in the SI.

D3 dispersion corrections were calculated by the DFT-D3 software (version from 14th June 2016)\cite{53} for the PBE, HSE06, and PBE0 functionals using Becke-Johnson damping.\cite{55} A D3 dispersion correction optimized for the PBE0r functional was not available. The influence of D3 corrections for the PBE0r results will therefore be discussed on the basis of the D3 corrections for the PBE, HSE06, and PBE0 functionals.

### IV. RESULTS AND DISCUSSION

#### A. Magnetic Order

The experimentally determined atomic structures referenced in Sec.\[4\] were taken as starting geometry of the electronic structure calculations. The structures were optimized by the individual DFT functionals under the constraint of fixed lattice vectors which were taken from experimental data. For most of the systems the initial spin configurations were taken from the references mentioned in Sec.\[4\] or they were derived by projecting the given non-collinear spins onto a collinear arrangement. Otherwise, a search for the minimum energy spin configuration was performed. The procedure for identifying the minimum energy spin configuration as well as the classification of the \( \text{ls-Mn}_{\text{III}} \) and \( \text{Mn}_{\text{IV}} \) ions is described in the SI. The
initial spins were fully optimized including a possible re-ordering – but no spin-flips – in the subsequent electronic structure calculations.

The spin configuration of cubic LiMn$_2$O$_4$ was investigated in several previous theoretical and experimental studies$^{[7] [9] [10] [58] [59]}$ which showed that the corner-sharing (MnO$_6$)$_4$ tetrahedra, formed for example by the four upper left Mn ions shown in FIG. 3, generally contain two Mn$^{III}$ and two Mn$^{IV}$ ions. Furthermore, an antiferromagnetic long-range order at low temperatures was proposed. Our calculations confirm this result in that a ferromagnetic structure is energetically less stable then a proposed. Our calculations confirm this result in that a ferromagnetic structure is energetically less stable then a proposed.

The PBE0 energy difference between the PBE0r minimum configuration and the PBE0 minimum is 0.003 eV per atom and thus very small. In conclusion, the energy differences are one order of magnitude smaller than the error of the finite basis set (0.01 eV per atom) in all of these calculations. The latter is in the range of the experimental uncertainty for formation enthalpies.$^{[60] [61]}$

Therefore, the two magnetic orders in FIG. 3 can be considered as degenerate within the given accuracy.

FIG. 3 illustrates the lowest-energy oxidation and spin states of the Mn atoms in LiMn$_2$O$_4$ obtained by PBE0r (a) as well as by PBE0 and HSE06 (b). The size and color represent the position of Mn in the $z$ direction of the unit cell: from large/bright (top layer) to small/dark (bottom layer). The Roman numerals correspond to the oxidation states. Filled and empty circles represent the two spin channels. The lines define the (MnO$_6$)$_4$ tetrahedra.

FIG. 4. The lowest-energy oxidation and spin states of the Mn ions calculated by the hybrid functionals. First of all, we note that there are many other configurations with very similar energies differing only by a few meV per atom. While the PBE0 and HSE06 calculations yield the same configuration, the result obtained in the PBE0r calculations differs slightly. Both configurations have in common that the spins of the Mn ions are ordered in antiferromagnetically coupled (100) planes (planes of filled and empty circles in FIG. 3). Moreover, in each plane there is an equal number of Mn$^{III}$ and Mn$^{IV}$ ions. Additionally, all (MnO$_6$)$_4$ tetrahedra consist of two Mn$^{III}$ and two Mn$^{IV}$ ions. This is in agreement with the previous studies mentioned above. However, the distribution of Mn atoms with different oxidation states within the network of tetrahedra is not the same in PBE0 and HSE06 on the one hand and PBE0r on the other hand. Still, the second lowest minimum found by HSE06 is the minimum of PBE0r. The total energy difference between these two spin configurations is only 0.002 eV per atom, which is within the remaining uncertainty of the hybrid functionals. The PBE0r minimum configuration is also among the energetically lowest configurations of PBE0.

FIG. 4. The lowest-energy oxidation and spin states of the Mn ions calculated consistently by all hybrid functionals for (a): $\lambda$-Mn$_2$O$_4$ and (b): Li$_{0.5}$Mn$_2$O$_4$. The size and color represent the position of Mn in the $z$ direction of the unit cell: from large/bright (top layer) to small/dark (bottom layer). The Roman numerals correspond to the oxidation states. Filled and empty circles represent the two spin channels. The lines define the (MnO$_6$)$_4$ tetrahedra.
B. Formation Energies

Arguably, the most important benchmark property is the relative stability of different structures. In particular, formation energies $\Delta E_f$ can be compared to other levels of theory and to experimental formation enthalpies $\Delta H_f$ to judge the quality of a given exchange-correlation functional. The formation energy is defined as the difference between the total energy of a given structure and the sum of the total energies of the elements in their reference modification, i.e. $H_2(g)$, $O_2(g)$, bulk bcc Li, and bulk $\alpha$-Mn in the present case. In contrast to formation energies, experimental formation enthalpies also include the zero point energy. Additionally, formation enthalpies are determined at standard conditions, i.e. at a temperature of 298.15 K and a pressure of 1 bar. However, the additional contributions are typically small compared to potential energy differences of different chemical compounds or structures. Therefore, comparing formation energies $\Delta E_f$ and standard formation enthalpies $\Delta H_f^0$ is a reasonable and frequently used approximation, which we will also employ here.

The calculated formation energies and the corresponding experimental formation enthalpies of the benchmark systems are given in TABLE I. The internal structures of the benchmark systems were optimized by the respective functionals under the constraint of fixed lattice vectors. The unit cell parameters were taken from the experimental data cited in Sec. [4]. The deviations between the theoretical and experimental results are plotted in FIG. [5]. First, the agreement between FHI-aims and CP-PAW calculations is investigated by performing PBE calculations with both codes. As shown in the columns PBE (FHI-aims) and PBE$_{PAW}$ (CP-PAW) of TABLE I, the agreement for the formation energies of the manganese oxides and water is very good. However, the formation energies of the lithium oxides show larger deviations of up to 0.13 eV per atom. This is mainly related to the description of the Li atoms, which is also visible in the deviations between the PBE formation energies for the lithium manganese oxides calculated with both codes. Also in this case the discrepancies increase with larger Li contents. Tests have shown that if the 1s electrons of Li would also have been treated as valence electrons in the CP-PAW calculations, the deviation, for example, for the Li$_2$O formation energy could have been reduced by 0.05 eV per atom. The PBE value from CP-PAW for the formation energy of Li$_2$O$_2$, which deviates by 0.10 eV per atom from the value obtained by FHI-aims, agrees within 0.02 eV per atom with the Vienna Ab initio Simulation Package (VASP) [64, 65]. For all benchmark systems except the lithium oxides the maximum deviation of the formation energies is 0.02 eV per atom, which is within the basis set error.

Irrespective of the DFT code, the PBE formation energies of all (lithium) manganese oxides are much smaller, i.e. less negative, than the experimental enthalpies. These systematic deviations have previously been explained by the self-interaction error of GGA functionals [45]. (Lithium) manganese oxides are highly correlated systems as the Mn d electrons are strongly localized. The size of the Mn 3d valence orbitals is similar to the size of the 3s and 3p core orbitals which leads to a strong Coulomb interaction. Those systems are typically most severely affected by the self-interaction error. Specifically, the energy of localized states is unphysically increased by the interaction of an electron with its own charge density. Therefore, delocalized charge distributions, i.e. metallic behavior, are favored. As a consequence, metallic Mn is more favored than oxidic Mn and consequently the formation energies of the (lithium) manganese oxides are smaller. The introduction of exact exchange contributions aims to reduce the self-exchange error, which results in a more accurate description of localized states. In conclusion, the formation energies of the (lithium) manganese oxides should be larger in case of hybrid functionals compared to the PBE GGA functional, which is consistent with our improved results for the oxide benchmark systems reported in TABLE [4].

The results of the PBE0 and HSE06 functionals are very similar. Therefore, the exclusion of the long-range exact exchange contributions seems to be a good approximation leading only to small errors. However, both functionals overestimate the formation energies of all (lithium) manganese oxides compared to the experimental values, while PBE underestimates the formation energies. Therefore, a HF mixing factor between 0 and 25% should improve the agreement with experiment. This is the case for PBE0r, which uses only 9% HF on-site exchange for Mn while off-site exchange terms are described by GGA only, and indeed we find a better agreement with the experimental data of the (lithium) manganese oxides as shown in FIG. [5].

The freedom of choosing the amount of on-site exact exchange allows – to a certain extent – to compensate for errors introduced by the local approximation leading only to small errors. However, other functionals overestimate the formation energies of all (lithium) manganese oxides compared to the experimental values, while PBE underestimates the formation energies. Therefore, a mixing factor between 0 and 25% should improve the agreement with experiment. This is the case for PBE0r, which uses only 9% HF on-site exchange for Mn while off-site exchange terms are described by GGA only, and indeed we find a better agreement with the experimental data of the (lithium) manganese oxides as shown in FIG. [5].

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TABLE I. Calculated formation energies $\Delta E_f$ and experimental standard formation enthalpies $\Delta H_f^\circ$ in eV per formula unit for the investigated benchmark systems. The structures were optimized under the constraint of fixed lattice vectors which were taken from experimental data. The mean absolute error (MAE) compared to the experimental data is given for each functional.

| System          | PBE  | PBE$_{PAW}$ | PBE0 | HSE06 | PBE0r | Exp. |
|-----------------|------|-------------|------|-------|-------|------|
| $\text{H}_2\text{O}(\text{g})$ | -2.49 | -2.52       | -2.64 | -2.63 | -2.38 | -2.51$^{[62]}$ |
| $\text{H}_2\text{O}(\text{l})_\text{h}$ | -3.19 | -3.19       | -3.28 | -3.29 | -3.03 | -2.96$^{[62]}$ |
| $\text{Li}_2\text{O}_2$     | -5.79 | -6.18       | -5.99 | -5.98 | -5.91 | -5.66$^{[63]}$ |
| $\text{Li}_2\text{O}$       | -5.60 | -6.00       | -5.88 | -5.87 | -5.78 | -6.21$^{[62]}$ |
| $\text{MnO}$              | -2.54 | -2.58       | -4.49 | -4.46 | -3.75 | -3.99$^{[62]}$ |
| $\text{Mn}_3\text{O}_4$     | -11.56 | -11.61     | -16.00 | -16.05 | -14.30 | -14.38$^{[62]}$ |
| $\alpha\text{-Mn}_2\text{O}_3$ | -8.35 | -8.35       | -10.91 | -10.98 | -9.95 | -9.94$^{[62]}$ |
| $\beta\text{-Mn}_2\text{O}_3$ | -5.07 | -5.07       | -5.51 | -5.61 | -5.51 | -5.39$^{[62]}$ |
| LiMnO$_2$             | -7.48 | -7.56       | -8.98 | -8.99 | -8.31 | -8.70$^{[60]}$ |
| $\lambda\text{-Mn}_3\text{O}_4$ | -9.81 | -9.81       | -10.60 | -10.71 | -10.76 | — |
| Li$_4$Mn$_2$O$_4$      | -11.58 | -11.65     | -12.81 | -12.91 | -12.55 | — |
| Li$_2$Mn$_2$O$_4$      | -13.15 | -13.26     | -14.91 | -14.98 | -14.30 | -14.32$^{[61]}$ |
| Li$_2$Mn$_2$O$_4$      | -15.18 | -15.36     | -18.07 | -18.09 | -16.78 | -17.34$^{[60]}$ |

| MAE   |       |       |       |       |       | 1.13 |
|-------|-------|-------|-------|-------|-------|------|
| MAE / atom | 0.25 | 0.22  | 0.13  | 0.13  | 0.07  | 0.25 |

FIG. 5. Differences between calculated formation energies and experimental standard formation enthalpies $\Delta E_f - \Delta H_f^\circ$ in eV per formula unit for the benchmark systems obtained by the investigated functionals. The energy axis is inverted to show overestimated formation energies above the zero line and underestimated formation energies below. All calculated formation energy values and standard formation enthalpies are given in TABLE I.

point energy and are thus expected to be too high. Since the contribution of the experimental zero point energy is about 0.24 eV$^{[70]}$, the experimental formation energy at 0 K without zero point energy correction is $-2.72$ eV. Thus, the PBE0 and HSE06 results are more accurate for the formation energy of the $\text{H}_2\text{O}$ monomer. The less accurate result of PBE0r could be caused by the lack of off-site exact exchange, which is important for the covalent bonds in $\text{H}_2$, $\text{O}_2$, and $\text{H}_2\text{O}$. The zero point energies are typically much smaller if no H atoms are present in the system.

The PBE0r approximation of on-site exchange should work best for oxides. To check this hypothesis, formation energies $\Delta E_{\text{ox}}$ and experimental standard formation enthalpies $\Delta H_{f\text{ox}}$ have also been calculated with respect to a reference of the oxides $\text{Li}_2\text{O}$, $\text{MnO}$, and $\beta$-$\text{Mn}_2\text{O}_3$ instead of the elemental reference states for the investigated benchmark systems (TABLE I). Therefore, these energy differences do not include information from the covalently bonded $\text{H}_2$, $\text{O}_2$, and $\text{H}_2\text{O}$ and metallic Li and $\alpha$-$\text{Mn}$, which are most critical in case of the PBE0r functional. Again, the results of PBE0 and HSE06 are overall very similar with a slightly smaller mean absolute error (MAE) of the HSE06 results compared to experimental...
TABLE II. Formation energies $\Delta E_{\text{ox}}$ and experimental standard formation enthalpies $\Delta H_{\text{ox}}^\circ$ for the investigated benchmark systems calculated with respect to the oxides $\text{Li}_2\text{O}$, $\text{MnO}$, and $\beta$-$\text{Mn}_2\text{O}_3$ in eV per formula unit. The structures were optimized under the constraint of fixed lattice vectors, which were taken from experimental data. As expected, the PBE0r results now show a much reduced MAE of 0.13 eV which is about 2.5 times smaller than the MAE for the other two hybrid functionals. In general, the MAEs for the formation energies with respect to the oxides are almost half of the MAEs for the formation energies from the elements (TABLE II) in the case of all hybrid functionals.

In summary, the MAE of the formation energies from the elements for all benchmark systems can be reduced from 1.13 eV (PBE) to 0.57 eV (PBE0) by the inclusion of 25% HF exchange confirming that the inclusion of exact exchange is very important for these systems. However, this increases the average computation time of the benchmark systems by a factor of about 25. The MAE is only very little affected by the neglect of the long-range exact exchange terms (PBE0 vs. HSE06). This decreases the computational effort of HSE06 compared to PBE0 by a factor of 0.8. The MAE can further be decreased to 0.25 eV (PBE0r) for these benchmark systems if smaller HF mixing factors are used. For the formation energy with respect to reference oxides the MAE of the PBE0r functional is only 0.13 eV providing the best agreement with the experimental data and demonstrating a very good description of energy differences. However, the main advantage of the PBE0r functional is that the average computation time per iteration of the benchmark systems compared to PBE$_{\text{PAW}}$ is only increased by a factor of 1.3 while the error is reduced by a factor of 4.

C. Intercalation Potential

An important property of the $\text{Li}_x\text{Mn}_2\text{O}_4$ spinel is the possibility to remove or incorporate Li atoms by (de)intercalation. This enables the application as cathode material for lithium ion batteries. Experiments show that the standard electrochemical potential of a $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ cell is about 4 V vs. Li/Li$^+$ in the range of $0 \leq x \leq 1$ and 3 V in the range of $1 < x \leq 2$.\[71\]

The intercalation potential $\Delta G_p$ can be calculated by

$$\Delta G_p = (x_2 - x_1)G_{\text{Li}} + G_{\text{Li}_1\text{Mn}_2\text{O}_4} - G_{\text{Li}_2\text{Mn}_2\text{O}_4}$$

where $x_1$ and $x_2$ specify the Li content of the $\text{Li}_x\text{Mn}_2\text{O}_4$ structure.\[72\] It corresponds to the Gibbs free energy difference of the reaction

$$\text{Li}_{x_2}\text{Mn}_2\text{O}_4 \rightleftharpoons \text{Li}_{x_1}\text{Mn}_2\text{O}_4 + (x_2 - x_1)\text{Li}$$

divided by $(x_2 - x_1)$. The Gibbs free energy $G$ can be approximated by the total energy $E$ when neglecting the influence of zero point energies and entropic contributions at finite temperatures. The resulting error of this approximate treatment is typically small for this reaction since the change in the neglected terms is much smaller than the change in the total energy $E$ during this reaction.\[72\]

If the intercalation potential of $\text{Li}_2\text{Mn}_2\text{O}_4$ is calculated from the experimental formation enthalpies given in TABLE I, the result is an intercalation potential of 3.02 eV which matches the electrochemically determined data given in TABLE III very well.

The experimentally measured standard electrochemical potentials vs. Li/Li$^+$ $E_p^0$ are in between the calculated PBE and PBE0 intercalation potentials $E_p$ (TABLE III). The MAE of the three PBE0 intercalation potentials with respect to the experiment is 0.27 eV and thus much smaller than the MAE of PBE, which is 0.73 eV. The HSE06 results exhibiting an MAE of 0.22 eV are only a little closer to the experimental data than PBE0. As expected, the PBE0r values (MAE 0.50 eV) are in between the PBE and PBE0 data, but only slightly better than PBE and clearly less accurate than PBE0 and HSE06. Still, the trend of the intercalation potential as a function of the Li content $x$ is described reliably by PBE0r in contrast to PBE which predicts the relative differences among the potentials at different lithium contents inaccurately. PBE0 and HSE06 describe the relative differences well but not as good as PBE0r whose results show a relatively constant underestimation of approximately 0.5 eV for all potentials.

D. Structural Properties

Up to this point, all properties have been obtained from optimized atomic positions using the experimental lattice parameters. A natural next question is how
well the tested functionals are able to describe the structural and structure-related properties such as the equilibrium lattice constants and bulk moduli. To answer this question, we used the Birch-Murnaghan equation of state \cite{Birch:1947, Murnaghan:1948}

\[
U = U_0 + \frac{9}{2}B_0V_0 \left[ \left( \frac{V}{V_0} \right)^\frac{2}{3} - 1 \right]^2 \\
\left\{ B'_0 \left[ \left( \frac{V}{V_0} \right)^\frac{2}{3} - 1 \right] - 4 \left( \frac{V}{V_0} \right)^\frac{2}{3} + 6 \right\},
\]

(7)
to derive the equilibrium energy \(U_0\), equilibrium volume \(V_0\), the bulk modulus at zero pressure \(B_0\), and its pressure derivative \(B'_0\). To reduce the search space, in case of non-cubic cells we have kept the ratios of the lattice parameters and scaled the experimental lattice constants isotropically by factors in the range from 0.95 to 1.05 in steps of 0.01. Again, for each calculation the atomic positions in the cells were optimized under the constraint of the respective lattice constants.

Approximating the internal energy \(U\) by the total energy \(E\), the Birch-Murnaghan equation of state describes the \(E(V)\) relation for all periodic benchmark systems very well. The formation energies using the oxides \(\text{Li}_2\text{O}\), MnO, and \(\beta\text{-MnO}_2\) as reference were calculated using the resulting equilibrium energies \(E_0\) from the Birch-Murnaghan equation of state for each hybrid functional. The values are given in the SI. These energies deviate only very little from the DFT data using the experimental lattice constants, which are given in TABLE II. The MAE of the energies per formula unit changes only by 0.009 eV for PBE0, −0.001 eV for HSE06, and −0.013 eV for PBE0r.

TABLE IV shows the relative deviations between the calculated equilibrium lattice constants and the experimental data. In contrast to the formation energies, the PBE equilibrium lattice constants do not show large deviations from the experimental data with an overall relative error of only 0.6%, which is in agreement with the general finding that structural properties are well described already at the GGA level. PBE0 and HSE06, which have a tendency to only very slightly underestimate the lattice parameters, yield an even smaller error as low as 0.2% with respect to experiment. This is reasonable as the experimental results were determined at finite temperature, and should be somewhat higher than the theoretical results obtained at 0 K due to thermal expansion. PBE0r underestimates in particular the lattice constants of Li by 2.1%. The lattice constants of the lithium oxides are described with an accuracy comparable to the other hybrid functionals. The equilibrium lattice constants of all given (lithium) manganese oxides are overestimated between 0.7 and 1.5% thus covering a range of 0.8%. PBE0 and HSE06 span exactly the same range of 0.8% (from −0.7 to 0.1 and from −0.6 to 0.2, respectively). Thus, the relative differences are described similarly by all hybrid functionals. Still, there is a constant shift of about 1% to larger lattice parameters with PBE0r compared to PBE0 and HSE06. Consequently, this leads to a mean relative error of approximately 1.0% for PBE0r which is still a very good agreement. We attribute the overestimation of the lattice constants to the neglect of off-site HF exchange terms which we expect to strengthen bonds. The equilibrium bond lengths for the molecular systems are reported in the SI. The results for \(\alpha\text{-Mn}\) are not listed in TABLES IV and V because no minimum is observed in the isotropic compression/expansion range from 0.95 to 1.05 using any of the hybrid functionals. If the equilibrium lattice constant is calculated by PBE with collinear spin, the outcome is an underestimation of 2.7%, which is very similar to a previous PBE study employing non-collinear spin.\cite{Lee:2006}

The error of PBE0, HSE06, and PBE0r could originate from the restriction to a collinear spin arrangement in our calculations, as \(\alpha\text{-Mn}\) has a complex non-collinear magnetic electronic structure, whose characterization is beyond the scope of the present work due to the large computational effort.

The calculated and experimental bulk moduli \(B_0\) are given in TABLE V PBE generally underestimates the bulk moduli except for the bulk modulus of Li, with an overall MAE of about 13 GPa. PBE0 matches the experimental results with a MAE of only 7 GPa very well, and except for \(\beta\text{-MnO}_2\) the bulk modulus is typically overestimated. However, this comparison between theory and experiment has to be made with care, as in contrast to formation energies and lattice constants that can be measured quite accurately, the experimental bulk moduli have larger uncertainties. Especially, in the case of \(\beta\text{-MnO}_2\) the experimental values of the bulk modulus in the literature show large differences depending on the method which was used.\cite{Hernandez:2010} From our calculations the reported value of 260 GPa fits the trend that the experimental values are between the PBE and PBE0 results better. The HSE06 results are again very similar to the PBE0 results, promoting the general use of HSE06 instead of PBE0 for these types of systems because the same accuracy is obtained with less computational effort.

TABLE IV. Relative deviations between the experimental equilibrium lattice constants and the calculated values using the examined functionals in %.

| System          | PBE | PBE0 | HSE06 | PBE0r |
|-----------------|-----|------|-------|-------|
| Li              | −0.9| 0.0  | −0.3  | −2.7  |
| \(\text{Li}_2\text{O}\) | 0.9 | −0.4 | −0.4  | −0.1  |
| \(\text{Li}_2\text{O}\) | 0.8 | −0.5 | −0.4  | −0.5  |
| MnO             | 0.1 | −0.1 | 0.1   | 1.0   |
| \(\text{Mn}_2\text{O}_4\) | 0.3 | 0.0  | 0.1   | 1.3   |
| \(\alpha\text{-Mn}_2\text{O}_3\) | 0.5 | 0.0  | 0.1   | 1.5   |
| \(\beta\text{-MnO}_2\) | 0.3 | −0.7 | −0.6  | 0.7   |
| Li\(\text{MnO}_2\) | 1.1 | 0.1  | 0.2   | 1.1   |
| \(\lambda\text{-Mn}_2\text{O}_3\) | 0.7 | −0.4 | −0.2  | 1.2   |
| \(\text{LiO}_2\text{Mn}_2\text{O}_4\) | 0.2 | −0.1 | 0.0   | 1.1   |
| Li\(\text{Mn}_2\text{O}_4\) | −0.2 | −0.1 | 0.1   | 0.8   |
| \(\text{Li}_2\text{Mn}_2\text{O}_4\) | 0.7 | 0.0  | 0.1   | 0.9   |
| Mean Error      | 0.6 | 0.2  | 0.2   | 1.0   |
TABLE V. Calculated and experimental bulk moduli \( B_0 \) in GPa for the benchmark systems. The bulk modulus of \( \beta\text{-MnO}_2 \) has not been included in the calculation of the MAE with respect to experiment because of the large uncertainty in the experimental value.

| System | PBE | PBE0 | HSE06 | PBE0r | Exp. |
|--------|-----|------|-------|-------|------|
| Li       | 13  | 13   | 13    | 14    | 12\cite{28} |
| Li\(_2\)O\(_2\) | 72  | 79   | 79    | 76    | —    |
| Li\(_3\)O    | 74  | 82   | 81    | 80    | 82\cite{79} |
| MnO      | 124 | 162  | 161   | 148   | 154\cite{80} |
| Mn\(_2\)O\(_4\) | 127 | 149  | 149   | 131   | 133\cite{81} |
| \(\alpha\)-Mn\(_2\)O\(_3\) | 140 | 173  | 173   | 151   | 169\cite{82} |
| \(\beta\)-Mn\(_2\)O\(_2\) | 224 | 263  | 262   | 229   | 260\cite{83} |
| Li\(_2\)Mn\(_2\)O\(_4\) | 111 | 127  | 127   | 112   | —    |
| \(\lambda\)-Mn\(_2\)O\(_4\) | 100 | 119  | 118   | 100   | —    |
| Li\(_2\)Mn\(_2\)O\(_4\) | 108 | 126  | 126   | 108   | —    |
| Li\(_2\)\(_2\)Mn\(_2\)O\(_4\) | 118 | 129  | 133   | 126   | 119\cite{84} |
| Li\(_2\)\(_3\)Mn\(_2\)O\(_4\) | 114 | 129  | 129   | 115   | —    |
| MAE     | 13  | 7    | 7     | 6     | —    |

For the PBE0r results we would expect that the values of the oxide benchmark systems are in between the results of PBE and PBE0, which is indeed confirmed. The PBE0r MAE of 6 GPa is similar to the ones of PBE0 and HSE06 and thus in very good accordance with the experimental measurements.

All four functionals predict that the bulk modulus increases upon lithiation of Li\(_2\)Mn\(_2\)O\(_4\) in the range \(0 \leq x \leq 1\). The bulk modulus of tetragonal Li\(_2\)Mn\(_2\)O\(_4\) is however predicted to be smaller than the one of LiMn\(_2\)O\(_4\) with the exception of the PBE0 bulk modulus of Li\(_2\)Mn\(_2\)O\(_4\) which is equal to the one of LiMn\(_2\)O\(_4\).

E. Band Gaps

Important properties in electronic applications and in optical absorption are the indirect and direct band gaps, respectively. The indirect band gap is the smallest overall energetic difference between occupied and unoccupied states. For the direct band gap, the differences between highest occupied and lowest unoccupied state are individually calculated for each \(k\)-point, and then the minimum of those is determined. The calculated direct band gaps are given in TABLE VI and compared to spectroscopic data. In case of the molecular systems, the first spin-allowed electronic transition is considered.

Based on the results of Sec. IV B we have already concluded that the self-interaction error is much larger for PBE than for the hybrid functionals. Strong self-interaction leads to a prediction of a too small or even non-existent band gap\cite{45,93} since localized electrons become less favored, resulting in an increased metallicity of the system. The data in TABLE VI confirms this trend. The band gaps calculated by PBE are generally smaller than those calculated by PBE0. The PBE band gaps of all given oxides are underestimated with respect to experiment. Some of the (lithium) manganese oxides are even predicted to be metallic, while the PBE0 functional correctly predicts their non-metallic character. However, the band gaps of all benchmark systems are always overestimated by PBE0 compared to the experimental data. The MAE is 1.9 eV. Despite the similar description of energetic and structural properties by PBE0 and HSE06, HSE06 predicts for all of these systems smaller band gaps which are in better agreement with experiment exhibiting a MAE of 1.2 eV only.

As PBE underestimates the band gaps while PBE0 yields too large band gaps, there should be an intermediate HF mixing factor which leads to a very good agreement with experiment as in the case of the formation energies (Sec. IV B). We tested different values for the HF mixing factor of Mn in the PBE0r functional and we experienced that increasing the HF mixing factor of Mn opens the band gap of the (lithium) manganese oxides. For example, in the range from 5 to 10% of the HF mixing factor the band gap of LiMn\(_2\)O\(_4\) widens from 0.7 to 1.2 eV. The chosen intermediate value of 9% does not only lead to a good prediction of the formation energies, but it also yields very accurate band gaps. The MAE for the band gaps of the (lithium) manganese oxides is only 0.3 eV, and the individual values are, as expected, in between the PBE and PBE0 gaps. For the covalently bonded systems this trend is not present. This again confirms that the approximation of the PBE0r functional is not well-suited for covalent bonds, but performs very well for the (lithium) manganese oxides. The MAE of PBE0r for all given systems is 1.0 eV which is the best agreement for the given functionals.

F. Density of States

The Kohn-Sham density of states (DoS) \(D(\epsilon)\) provides detailed insights into the electronic structure of a sys-
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tem, and, for example, the influence of Li insertion can be studied. Furthermore, some features like band gaps or orbital occupations can be directly compared to experimental data.

First, we will compare the DoS of LiMn$_2$O$_4$ calculated by PBE, PBE0, HSE06, and PBE0r (FIG. 6 and 7) in order to understand why the PBE results are less accurate than the results of the hybrid functionals (more information on the calculation procedure of the DoS in both DFT codes are given in the SI). Afterwards, we will study the effect of Li insertion on the electronic structure using the PBE0r DoS of Li$_x$Mn$_2$O$_4$ with $x = 0, 0.5, 1,$ and 2 (FIG. 7b and 8). In FIG. 6, 7, and 8 the peaks of the DoS are broadened for visualization which is done differently by FHI-aims and CP-PAW and must be considered in the comparison. All figures show only the DoS of one spin channel since the DoS of the other spin channel is identical for these optimized structures. The individual contributions of Mn d orbitals are shown separately for each atom in the unit cell.

The PBE DoS calculated by FHI-aims (FIG. 6 (a)) and CP-PAW (FIG. 7 (a)) are very similar. They reveal the missing band gap in those calculations. Furthermore, they show that all Mn atoms have the same electron density corresponding to an oxidation state of 3.5, i.e. the electrons are strongly delocalized. CP-PAW enables resolving the d electron density into the t$_{2g}$ and e$_g$ contributions, which are present in an octahedral ligand field. This reveals that all Mn d electrons have mainly t$_{2g}$ character. The underestimation of the stability of hs-states is again typical for self-interaction errors. In conclusion, PBE predicts metallic LiMn$_2$O$_4$ with all Mn being in the low-spin Mn$^{3.5}$ state. The MnO$_6$ octahedra are slightly distorted. The PBE PAW result shows that two Mn-O bonds are 1.94 Å and four are 1.97 Å. However, if this bond length difference is compared to the one of the JT distorted Mn$^{III}$ in case of the hybrid functionals mentioned later, it is obvious that this is not an accurate description of the JT distortion. The PBE outcome is contradicting experimental results which show that LiMn$_2$O$_4$ has a band gap and one half of the Mn is in the JT distorted hs-Mn$^{III}$ state while the other half is in the Mn$^{IV}$ state.

The DoS of the hybrid functionals (FIG. 6b and c and FIG. 7b) are very similar but clearly differ from the PBE DoS. The main effect of exact exchange is the self-interaction correction, which shifts filled electron levels downward. For manganese oxides this shifts the majority spin t$_{2g}$ states into the O 2p valence band. Similarly, it shifts the majority spin e$_g$ orbitals below the minority spin t$_{2g}$ orbitals and thus favors high-spin Mn.

FIG. 6. The density of states $D(\epsilon)$ of one spin channel plotted for the atoms in the LiMn$_2$O$_4$ unit cell calculated by (a): PBE, (b): PBE0, and (c): HSE06. Unoccupied orbitals are in lighter colors.
In particular PBE0 and HSE06 yield an almost equal DoS except for the size of the band gap. This is in accordance with the similar energetic and structural results. Hence, the reliability of the range-separated hybrid functional is again confirmed. The Mn d orbitals are split into two states of different energy due to the ligand field. In the PBE0r DoS this separation into the $t_{2g}$ and $e_g$ states is highlighted. The lower band is similar for each Mn since both Mn$^{III}$ and Mn$^{IV}$ have three $t_{2g}$ electrons. However, FIG. 7 shows that only half of the Mn in one spin channel in the LiMn$_2$O$_4$ unit cell (four of eight) have an $e_g$ electron which corresponds to the energetically highest occupied band. Thus, there are two different types of Mn in the LiMn$_2$O$_4$ unit cell: eight Mn$^{III}$ and eight Mn$^{IV}$ (in both cases four with spin up and four with spin down). Separately plotted DoS for both Mn states are given in the SI. They show that the $t_{2g}$ and $e_g$ electrons of a Mn have always the same spin direction, i.e. the Mn is in the hs-state. The hs-Mn$^{III}$ leads to a JT distortion of the corresponding MnO$_6$ octahedron.

A geometrical study of the structure which was optimized by PBE0 or HSE06 using the experimental lattice parameters, i.e. a cubic unit cell, shows that two Mn-O bonds are 1.92 Å, two are 2.05 Å, and two are 2.07 Å for the MnO$_6$ octahedra of Mn$^{III}$. PBE0r predicts the averaged bond distances 1.93 Å, 2.05 Å, and 2.10 Å respectively for these bonds. These confirm the presence of a JT distortion. The MnO$_6$ octahedra of the Mn$^{IV}$ are not JT distorted. PBE0 and HSE06 predict two Mn-O bond lengths of 1.89 Å and four of 1.90 Å, i.e. the MnO$_6$ octahedron is only very slightly distorted for Mn$^{IV}$. PBE0r yields for these bond lengths the averaged values 1.89 Å and 1.94 Å. The Mn-O bond lengths also show that the MnO$_6$ octahedra of Mn$^{III}$ are larger than those of Mn$^{IV}$ because of the additional $e_g$ electron of Mn$^{III}$ in the antibonding Mn-O orbital. All these features of the DoS of the hybrid functionals are in accordance with experimental results.

The Li$_x$Mn$_2$O$_4$ structure does not undergo any structural transformations if the Li content is varied in the range $0 \leq x \leq 1$. Only the lattice constant and the number of JT distorted MnO$_6$ octahedra decrease with decreasing Li content. Thus, one would expect that the DoS changes only slightly except for the number of $e_g$ electrons. This is confirmed by the data shown in FIG. 7 (b) and 8 (a) and (b). The number of $e_g$ electrons is in all cases equal to the number of Li$^+$ ions. There is no Mn$^{III}$ present in λ-Mn$_2$O$_4$. As a consequence, the band gap of λ-Mn$_2$O$_4$ is much larger than the band gaps of Li$_x$Mn$_2$O$_4$ with $0 < x \leq 1$: the transition in λ-Mn$_2$O$_4$ takes an electron from the oxygen valence band to the unoccupied d orbitals, while in Li$_x$Mn$_2$O$_4$ the transition is determined by the much smaller JT splitting of the $e_g$ states.

The DoS of Li$_2$Mn$_2$O$_4$ (FIG. 8 (c)) differs more from the DoS of Li$_x$Mn$_2$O$_4$ with $0 < x \leq 1$ because the unit cell is tetragonally distorted. However, the trend of the increasing number of $e_g$ electrons is retained. All Mn in the unit cell have one $e_g$ electron which means that they are all in the Mn$^{III}$ state. The JT distortion opens a gap between both $e_g$ states of the same spin channel. These two states are the highest occupied and lowest unoccupied state for Mn$^{III}$. This is shown in the DoS of one Mn$^{III}$ which is given in the SI. In Li$_x$Mn$_2$O$_4$ only Mn$^{III}$ ions are present and the entire structure is tetragonally distorted. Therefore, the band gap is larger than for Li$_2$Mn$_2$O$_4$ with $0 < x \leq 1$ because only strongly JT distorted Mn$^{III}$ are present. Moreover, the JT distortion decreases the difference between the $t_{2g}$ and $e_g$ state. This trend is also observed if we compare FIG. 7 (b) with FIG. 8 (c).
FIG. 8. The PBE0r density of states $D(\epsilon)$ of one spin channel plotted for the atoms (a): in the $\lambda$-Mn$_2$O$_4$ unit cell (48 atoms), (b): in the Li$_{0.5}$Mn$_2$O$_4$ unit cell (52 atoms), and (c): in the Li$_2$Mn$_2$O$_4$ unit cell (32 atoms). Unoccupied orbitals are shown in lighter colors.

The DoS of the various (lithium) manganese oxides can be analyzed in a similar way. The hs-Mn state is preferred for all given systems by the hybrid functionals. The PBE0r spin values of the Mn, from which one can derive their oxidation states, are given in the SI.

G. Dispersion Correction

None of the functionals investigated in this work includes long-range dispersion interactions explicitly. However, for a lot of systems, for example liquid water, the long-range dispersion interaction is crucial.\cite{94} Therefore, a dispersion correction scheme usable for (lithium) manganese oxides is needed in a study of the liquid-solid interface between water and a (lithium) manganese oxide. Several correction schemes have been suggested in the literature to overcome the limitation of present GGA and hybrid functionals. However, the currently available schemes were not benchmarked on systems as the (lithium) manganese oxides. We tested the prominent D3 correction suggested by Grimme.\cite{39} We will show that this dispersion correction can improve some combinations of systems and functionals but it also leads to artifacts in other combinations. Therefore, a general recommendation for the usage of the dispersion correction for (lithium) manganese oxides cannot be given. That is why we did not include the dispersion correction already in the results of the previous chapters.

The specific parameters of the D3 correction depend on the employed exchange-correlation functional to avoid double-counting of short-range dispersion interactions which are usually well described in DFT. The D3 dispersion corrections for the PBE, PBE0, and HSE06 functionals are relatively similar for all benchmark systems (see SI). Since PBE0r has been developed rather recently and therefore is not yet widely distributed, specific D3 parameters are not available for this functional. However, PBE, PBE0, HSE06, and PBE0r are all based on the same GGA, while only the exact exchange contributions are treated differently. Hence, PBE0r can be considered as interpolation between PBE and PBE0 with an in spirit similar but stronger approximation as in HSE06. Consequently, a suitable PBE0r D3 correction can be expected to be similar to those of the other three functionals. The errors of the PBE0r formation energies with respect to the experimental formation enthalpies are reduced most if the D3 correction is included employing the parameters for the HSE06 functional. The MAE of $\Delta E_f$ decreases from 0.25 to 0.13 eV. Therefore, this D3 correction is applied for PBE0r calculations in the remaining part of this work. The D3 corrected values of $\Delta E_f$, $\Delta E_{ox}$, and $\Delta E_p$ using the HSE06 and PBE0r functionals are given in the SI.

The influence of the dispersion correction is larger for the systems containing Li. In particular, the formation energies of the lithium oxides are highly improved, while the manganese oxides are not much affected by the dispersion
correction. Since the dispersion correction leads in most cases to larger, i.e. more negative, formation energies and HSE06 already tends to overestimate the formation energies, the MAE of $\Delta E_1$ is increased from 0.59 to 0.65 eV for HSE06. However, the MAE of $\Delta E_{\text{ox}}$ is reduced from 0.33 to 0.21 eV for HSE06. For PBE0r the MAE of $\Delta E_{\text{ox}}$ hardly changes from 0.13 to 0.15 eV. The intercalation potential of Li$_2$Mn$_2$O$_4$ is raised by the dispersion correction which improves the description in the case of PBE0r from a MAE of 0.50 to 0.28 eV. The accurate prediction of the trend of the potential as a function of the Li content is retained. For HSE06 the D3 correction increases the overestimation so that the MAE changes from 0.22 to 0.43 eV. In conclusion, the D3 dispersion correction improves the general agreement between PBE0r and experimental energetic properties.

We found that the D3 correction can introduce artifacts for some manganese oxides in the potential energy surface. An example is the $E(V)$ plot of MnO calculated by HSE06 plus the D3 dispersion correction (FIG. 9). Without the dispersion correction HSE06 predicts a parabolic behaviour of $E(V)$ close around the equilibrium volume as expected. However, adding the dispersion correction introduces an unphysical step of about 0.14 eV per atom into $E(V)$ around the equilibrium volume.

![FIG. 9. The energy $E(V)$ of MnO in eV per atom as a function of the unit cell volume $V$ in $\text{Å}^3$ calculated by HSE06 without and with D3 dispersion correction. The zero point of the energy axis is shifted to $E_{\text{HSE06}}(V_{\text{exp}})$. The dashed red line marks the experimentally measured unit cell volume $V_{\text{exp}}$.][28]

The phenomenon can be explained by the dependency of the D3 dispersion coefficients from the coordination number. In FIG. 10 the dependency of the D3 coefficients $C_6^{AA}$ of Mn is shown as an example. It is obvious that there is a large change in the dispersion coefficient around a coordination number of 5.76. Since the MnO equilibrium structure includes Mn with a coordination number inside this regime, small variations of the volume lead to large changes in the values of the used dispersion coefficients for Mn. These changes of the dispersion coefficients are not physically correct. Thus, this introduces an unphysical step in the potential energy surface.

![FIG. 10. The D3 dispersion coefficient $C_6^{AA}$ of Mn in $E_{\text{HSE06}}(V_{\text{exp}})$ as a function of the coordination number. The violet diamonds mark the coordination numbers which are used in FIG. 9. The x-axis is inverted for a direct comparison with FIG. 9. The dashed red line marks the coordination number which is present in the experimentally measured MnO structure.][28]

Also in the case of Mn$_3$O$_4$ and $\alpha$-Mn$_2$O$_3$ sudden drops in the D3 corrected $E(V)$ plots are observed if the lattice constants are scaled by a factor between 0.95 and 1.05 since the coordination numbers of Mn are above and below the step shown in FIG. 10. The given change of the D3 dispersion coefficients $C_6$ and $C_8$ as a function of the coordination number of Mn is included to assign different dispersion coefficients to the larger Mn$^{\text{III}}$ on the one hand and the smaller Mn$^{\text{II}}$ and Mn$^{\text{IV}}$ on the other hand or to tetrahedrally and octahedrally coordinated Mn. However, since the step can be close to the equilibrium geometry of some manganese oxides, it can introduce an unphysical step in the resulting potential energy surface. Regarding the structural properties, the D3 correction decreases the equilibrium lattice constants of Li$_x$Mn$_2$O$_4$, with $0 \leq x \leq 1$, by 0.8% in the case of PBE0r. This improves the agreement with experiment as the uncorrected lattice constants of the (lithium) manganese oxides were overestimated by about 1%. However, the lattice constants of the Li-rich Li$_2$Mn$_2$O$_4$ are underestimated by 0.8% compared to experiment if the D3 correction is applied. This is in contrast to the constant overestimation in the results of PBE0r without the dispersion correction. Other (lithium) manganese oxides which are not affected by the error introduced by the change of the dispersion coefficients with coordination number are $\beta$-Mn$_2$O$_3$ and LiMnO$_2$. For these two the relative deviation of the lattice constants from experimental data is reduced from 0.7% to 0.3% and 1.1% to 0.1%, respectively.

The D3 dispersion correction can improve some combinations of systems and functionals but it also leads to artifacts in other combinations. Therefore, it has to be carefully checked for the individual system if the D3 correction can be applied to a (lithium) manganese oxide. The correction does not yield better results for each of these systems. However, for other systems, for example liquid water, the D3 correction was found to provide a very accurate description. [94–97]
V. CONCLUSION

The PBE, PBE0, HSE06, and PBE0r exchange-correlation functionals have been benchmarked for various Li$_x$Mn$_y$O$_z$ systems. The deviations of predicted energetic, structural, and electronic properties from experimental data can in general be reduced by the inclusion of exact exchange contributions. Neglecting the long-range exact exchange terms is proven to be a very good approximation. The quality of the HSE06 results is very similar to that of the PBE0 results or even better in the case of band gaps. However, the average computation time per self-consistency cycle of the benchmark systems is reduced by a factor of 0.8 which makes the HSE06 functional preferable to the PBE0 functional for the given types of systems. The experimental formation energies, intercalation potentials, bulk moduli, and band gaps of the studied (lithium) manganese oxides are in between the PBE and PBE0 results. Consequently, an intermediate HF mixing factor as used in the PBE0r functional can further decrease the deviation in many cases. Due to the restriction of using only on-site HF exchange terms in PBE0r its average computation time per iteration of the benchmark systems is only increased by a factor of 1.3 compared to PBE$_\text{PAW}$, which is substantially less expensive than the PBE0 and HSE06 functionals. However, this approximation is not well-suited for strongly covalently bonded or metallic systems while it provides reliable results for highly correlated systems. Consequently, the accuracy of the results for the (lithium) manganese oxides is greatly improved. We conclude that PBE0r has the optimum cost-benefit ratio for these types of systems. In summary, the hybrid functionals PBE0, HSE06, and PBE0r agree well with experiment. The D3 dispersion correction suffers from a step like dependence on the coordination number, which produces unphysical behavior for some of the investigated systems.

Theoretical calculations for the lithium manganese oxide spinel Li$_x$Mn$_2$O$_4$, with 0 ≤ x ≤ 2, agree well with experimental results if hybrid functionals are used. The calculated formation energies, the trend of the intercalation potentials, the equilibrium lattice constants, the bulk moduli, and the band gaps are in accordance with experimental data. Several essentially degenerate antiferromagnetic states exist close to the energetically lowest configuration of Li$_x$Mn$_2$O$_4$. A formation of two oxidation states, +III and +IV, is observed for Mn. The Mn$^{3+}$ ions are in the hs-state and the corresponding MnO$_6$ octahedra are JT distorted.

ACKNOWLEDGMENTS

We thank the DFG (SFB 1073 project B03 and C03, project 217133147, project 405832858) for financial support. We gratefully acknowledge the funding of this project by computing time provided by the Paderborn Center for Parallel Computing (PC²). JB is grateful for a DFG Heisenberg professorship (BE3264/11-2, project 329898176).

[1] M. M. Thackeray, Manganese oxides for lithium batteries, Prog. Solid State Chem. 25, 1 (1997).
[2] H. Berg, K. Göransson, B. Noläng, and J. O. Thomas, Electronic structure and stability of the Li$_x$Mn$_2$O$_4$ (0 < x < 2) system, J. Mater. Chem. 9, 2813 (1999).
[3] J. Akimoto, Y. Tabakhashi, N. Kijima, and Y. Gotoh, Single-crystal X-ray structure analysis of the low temperature form of LiMn$_2$O$_4$, Solid State Ion. 172, 491 (2004).
[4] K. Momma and F. Izumi, VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data, J. Appl. Cryst. 44, 1272 (2011).
[5] J. M. Tarascon, W. R. McGinnon, F. Coowar, T. N. Bowmer, G. Amatucci, and D. Guyomard, Synthesis conditions and oxygen stoichiometry effects on Li insertion into the spinel LiMn$_2$O$_4$, J. Electrochem. Soc. 141, 1421 (1994).
[6] H. A. Jahn and E. Teller, Stability of polyatomic molecules in degenerate electronic states, Proc. Royal Soc. Lond. A 161, 220 (1937).
[7] C. Y. Ouyang, S. Q. Shi, and M. S. Lei, Jahn-Teller distortion and electronic structure of LiMn$_2$O$_4$, J. Alloy. Comp. 474, 370 (2009).
[8] P. Piszora, Temperature dependence of the order and distribution of Mn$^{3+}$ and Mn$^{4+}$ cations in orthorhombic LiMn$_2$O$_4$, J. Alloy. Comp. 382, 112 (2004).
[9] I. Tomeno, Y. Kasuya, and Y. Tsunoda, Charge and spin ordering in LiMn$_2$O$_4$, Phys. Rev. B 64, 094422 (2001).
[10] J. Sugiyama, T. Hiki, S. Noda, and M. Kontani, A $^7$Li-NMR study on spinel LiMn$_2$O$_4$: the evidence of an antiferromagnetic transition at 40 K, J. Phys. Soc. Jpn. 66, 1187 (1997).
[11] J. Maier, B. Pfeiffer, C. A. Volkert, and C. Nowak, Three-dimensional microstructural characterization of lithium manganese oxide with atom probe tomography, Energy Technol. 2016 4, 1565 (2016).
[12] L. Köhler, M. E. Abrishami, V. Roddatis, J. Geppert, and M. Risch, Mechanistic parameters of electrocatalytic water oxidation on LiMn$_2$O$_4$ in comparison to natural photosynthesis, ChemSusChem 10, 4479 (2017).
[13] S. K. Mishra and G. Ceder, Structural stability of lithium manganese oxides, Phys. Rev. B 59, 6120 (1999).
[14] A. van der Ven, C. Marianetti, D. Morgan, and G. Ceder, Phase transformations and volume changes in spinel Li$_x$Mn$_2$O$_4$, Solid State Ion. 135, 21 (2000).
[15] G. E. Grechnev, R. Ahuja, B. Johansson, and O. Eriksson, Electronic structure, magnetic, and cohesive properties of Li$_x$Mn$_2$O$_4$: Theory, Phys. Rev. B 65, 174408 (2002).
[16] V. L. Chevrier, S. P. Ong, R. Armiento, M. K. Y. Chan, and G. Ceder, Hybrid density functional calculations
of redox potentials and formation energies of transition metal compounds, Phys. Rev. B 82, 075122 (2010).

[17] C. Ouyang, H. Deng, Z. Ye, M. Lei, and L. Chen, Pulsed laser deposition prepared LiMn$_2$O$_4$ thin film, Thin Solid Films 503, 268 (2006).

[18] D. Hobbs and J. Hafner, Ab initio density functional study of phase stability and noncollinear magnetism in Mn, J. Phys.: Condens. Matter 13, L681 (2001).

[19] C. Franchini, R. Podloucky, J. Paier, M. Marsman, and G. Kresse, Ground-state properties of multivalent manganese oxides: Density functional and hybrid density functional calculations, Phys. Rev. B 75, 195128 (2007).

[20] E. Cockayne, I. Levin, H. Wu, and A. Llobet, Magnetic structure of bixbyte $\alpha$-Mn$_2$O$_3$: A combined DFT+U and neutron diffraction study, Phys. Rev. B 87, 184413 (2013).

[21] A. Yoshimori, A new type of antiferromagnetic structure in the rutile type crystal, J. Phys. Soc. Jpn. 14, 807 (1959).

[22] Y. Takahashi, J. Akimoto, Y. Gotoh, K. Dokko, M. Nishizawa, and I. Uchida, Structure and electron density analysis of lithium manganese oxides by single-crystal X-ray diffraction, J. Phys. Soc. Jpn. 72, 1483 (2003).

[23] M. Bianchini, F. Fauth, E. Suard, J.-B. Leriche, C. Masquelier, and L. Croguennec, Spinel materials for Li-ion batteries: new insights obtained by operando neutron and synchrotron X-ray diffraction, Acta Cryst. B 71, 688 (2015).

[24] A. Mosbah, A. Verbaere, and M. Tournoux, Phases Li$_3$MnO$_2$ rattlecahe au type spinelle, Mat. Res. Bull. 32, 1575 (1993).

[25] W. G. W. Wyckoff, Crystal Structures, 2nd edition ed. (Interscience, New York, 1963).

[26] H. Föppl, Die Kristallstrukturen der Alkaliperoxide, Z. anorg. allg. Chem. 291, 12 (1957).

[27] W. I. F. David, M. O. Jones, D. H. Gregory, C. M. Jewell, S. R. Johnson, A. Walton, and P. P. Edwards, A mechanism for non-stoichiometry in the lithium amide/lithium imide hydrogen storage reaction, J. Am. Chem. Soc. 129, 1594 (2007).

[28] D. Taylor, Thermal expansion data: I. Binary oxides with the sodium chloride and wurtzite structures, MO, Brit. Ceram. Trans. J. 83, 5 (1984).

[29] D. Jarosch, Crystal structure refinement and reflectance measurements of hausmannite, Mn$_3$O$_4$, Miner. Petrol. 37, 15 (1987).

[30] S. Geller, Structures of $\alpha$-Mn$_2$O$_3$, (Mn$_{0.98}$Fe$_{0.017}$)$_{203}$ and (Mn$_{0.37}$Fe$_{0.63}$)$_{203}$ and relation to magnetic ordering, Acta Cryst. B 27, 821 (1971).

[31] A. A. Bolzan, C. Fong, B. J. Kennedy, and C. J. Howard, Powder neutron diffraction study of pyroulsite, $\beta$-MnO$_2$, Aust. J. Chem. 46, 939 (1993).

[32] D. G. Kellerman, J. E. Medvedeva, V. S. Goshkov, A. I. Kurbakov, V. G. Zubkov, A. P. Tyutyunnik, and V. A. Trunov, Structural and magnetic properties of orthorhombic Li$_2$MnO$_2$, Solid State Sci. 9, 196 (2007).

[33] J. P. Perdew, M. Ernzerhof, and K. Burke, Rationale for mixing exact exchange with density functional approximations, J. Chem. Phys. 105, 9982 (1996).

[34] C. Adamo and V. Barone, Toward reliable density functional methods without adjustable parameters: The PBE0 model, J. Chem. Phys. 110, 6158 (1999).

[35] J. Heyd, G. E. Scuseria, and M. Ernzerhof, Hybrid functionals based on a screened Coulomb potential, J. Chem. Phys. 118, 8207 (2003).

[36] J. Heyd, G. E. Scuseria, and M. Ernzerhof, Erratum: "Hybrid functionals based on a screened Coulomb potential" [J. Chem. Phys. 118, 8207 (2003)], J. Chem. Phys. 124, 219906 (2006).

[37] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, Influence of the exchange screening parameter on the performance of screened hybrid functionals, J. Chem. Phys. 125, 224106 (2006).

[38] M. Sotoudeh, S. Rajpurohit, P. Blöchl, D. Mierwaldt, J. Norpoth, V. Roddatis, S. Mildner, B. Kressdorf, B. Ifland, and C. Jooss, Electronic structure of Pr$_{1-x}$Ca$_x$MnO$_3$, Phys. Rev. B 95, 235150 (2017).

[39] S. Grimmie, J. Antony, S. Ehrlich, and H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, J. Chem. Phys. 132, 154104 (2010).

[40] A. D. Fortes, I. G. Wood, D. Grigoriev, M. Alfredsson, S. Kipfstuhl, K. S. Knight, and R. I. Smith, No evidence for large-scale proton ordering in antarctic ice from powder neutron diffraction, J. Chem. Phys. 120, 11376 (2004).

[41] K. Burke, Perspective on density functional theory, J. Chem. Phys. 136, 155001 (2012).

[42] J. Neugebauer and T. Hickel, Density functional theory in materials science, WIRES 3, 438 (2013).

[43] R. Peverati and D. G. Truhlar, Review article: Quest for a universal density functional: the accuracy of density functionals across a broad spectrum of databases in chemistry and physics, Phil. Trans. R. Soc. A 372, 20120476 (2014).

[44] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77, 3865 (1996).

[45] C. J. Cramer and D. G. Truhlar, Density functional theory for transition metals and transition metal chemistry, Phys. Chem. Chem. Phys. 11, 10757 (2009).

[46] P. E. Blöchl, Projector augmented-wave method, Phys. Rev. B 50, 17953 (1994).

[47] P. E. Blöchl and C. Först, Node-less atomic wave functions, Pauli repulsion and systematic projector augmentation (2012), submitted, arXiv:1210.5937.

[48] P. E. Blöchl, Improved tetrahedron method for Brillouinzone integrations, Phys. Rev. B 49, 16223 (1994).

[49] P. E. Blöchl, Electrostatic decoupling of periodic images of plane-wave-expanded densities and derived atomic point charges, J. Chem. Phys. 103, 7422 (1995).

[50] R. Car and M. Parrinello, Unified approach for molecular dynamics and density-functional theory, Phys. Rev. Lett. 55, 2471 (1985).

[51] N. D. Mermin, Thermal properties of the inhomogeneous electron gas, Phys. Rev. A 137, 1441 (1965).

[52] V. Blum, R. Gehre, F. Hanke, P. Hauv, V. Hauv, X. Ren, K. Reuter, and M. Scheffler, Ab initio molecular simulations with numeric atom-centered orbitals, Comput. Phys. Commun. 180, 2175 (2009).

[53] C. G. Broyden, The convergence of a class of double-rank minimization algorithms I. General considerations, J. Inst. Math. Appl. 6, 76 (1970).

[54] R. Fletcher, A new approach to variable metric algorithms, Comput. J. 13, 317 (1970).
D. Goldfarb, A family of variable-metric methods derived by variational means. Math. Comp. 24, 23 (1970).

D. F. Shanno, Conditioning of quasi-Newton methods for function minimization. Math. Comp. 24, 647 (1970).

S. Grimme, S. Ehrlich, and L. Goerigk, Effect of the damping function in dispersion corrected density functional theory. J. Comput. Chem. 32, 1456 (2011).

J. Rodriguez-Carvajal, G. Rousse, C. Masquelier, and M. Hervieu, Electronic crystallization in a lithium battery material: Columar order of electrons and holes in the spinel LiMn2O4. Phys. Rev. Lett. 81, 4660 (1998).

Y.-I. Jang, B. Huang, F. C. Chou, D. R. Sadoway, and Y.-M. Chiang, Magnetic characterization of α-MnO2 and Li2Mn2O4 prepared by electrochemical cycling of LiMn2O4. J. Appl. Phys. 87, 7382 (2000).

M. Wang and A. Nadvotsky, LiMn2O4 (M = Mn, Fe, and Co): Energetics, polymorphism and phase transformation. J. Solid State Chem. 178, 1230 (2005).

D. M. Cupid, A. Reif, and H. J. Seifert, Enthalpy of formation of Li1+xMn2-xO4 (0 < x < 0.1) spinel phases, Thermochim. Acta 599, 35 (2015).

R. A. Robie, B. S. Hemingway, and J. R. Fisher, Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10^5 Pascals) Pressure and at Higher Temperatures (U.S. Geological Survey Bulletin, 1979).

https://janaf.nist.gov/tables/Li-018.html (1st August 2019).

M. K. Y. Chan, E. L. Shirley, N. K. Karan, M. Balasubramanian, Y. Ren, J. P. Greeley, and T. T. Fister, Structure of lithium peroxide, J. Phys. Chem. Lett. 2, 2483 (2011).

G. Kresse and J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B 54, 11169 (1996).

B. Ruscic, R. E. Pinzon, M. L. Morton, N. K. Srinivasan, M.-C. Su, J. W. Sutherland, and J. V. Michael, Active thermochemical tables: Accurate enthalpy of formation of hydroperoxyl radical, HO2, J. Phys. Chem. A 110, 6592 (2006).

D. Feller, K. A. Peterson, and B. Ruscic, Improved accuracy benchmarks of small molecules using correlation consistent basis sets, Theor. Chem. Acc. 133, 1407 (2014).

https://webbook.nist.gov/cgi/cbook.cgi?ID=C1333740&M=Mask=1000#Diatomic (1976), (1st November 2019).

https://webbook.nist.gov/cgi/cbook.cgi?ID=C7782447&M=Mask=1000#Diatomic (1977), (1st November 2019).

https://webbook.nist.gov/cgi/cbook.cgi?ID=C7732185&M=Mask=800#Electronic-Spec (1972), (1st November 2019).

R. J. Gummow, A. de Kock, and M. M. Thackray, Improved capacity retention in rechargeable 4V lithium/lithiummanganese oxide (spinel) cells, Solid State Ion. 69, 59 (1994).

M. K. Aydinol, A. F. Kohan, G. Ceder, K. Cho, and J. Joannopoulos, Ab initio study of lithium intercalation in metal oxides and metal dichalcogenides, Phys. Rev. B 56, 1354 (1997).

Y. Xia and M. Yoshio, An investigation of lithium ion insertion into spinel structure Li-Mn-O compounds, J. Electrochem. Soc. 143, 825 (1996).

D. Peramunage and K. M. Abraham, Preparation and electrochemical characterization of overlithiated spinel LiMn2O4. J. Electrochem. Soc. 145, 1131 (1998).

F. Birch, Finite elastic strain of cubic crystals, Phys. Rev. 71, 809 (1947).

F. D. Murnaghan, Finite deformations of an elastic solid, Am. J. Math. 59, 235 (1937).

D. Hobbs, J. Hafner, and D. Spivak, Understanding the complex metallic element Mn. I. Crystalline and non-collinear magnetic structure of α-Mn, Phys. Rev. B 68, 014407 (2003).

J. Trivisonno and C. S. Smith, Elastic constants of lithium-magnesium alloys, Acta Metall. 9, 1064 (1961).

S. Hull, T. W. D. Farley, W. Hayes, and M. T. Hutchings, The elastic properties of lithium oxide and their variation with temperature, J. Nucl. Mater. 160, 125 (1988).

D. W. Oliver, The elastic moduli of MnO, J. Appl. Phys. 40, 893 (1969).

J. Darul, C. Lathe, and P. Piszora, Mn2O4 under high pressure and temperature: Thermal stability, polymorphism, and elastic properties, J. Phys. Chem. C 117, 23487 (2013).

T. Yamanaka, T. Nagai, T. Okada, and T. Fukuda, Structure change of Mn2O3 under high pressure and pressure-induced transition, Z. Kristallogr. 220, 938 (2005).

J. Haines, J. M. Léger, and S. Hoyau, Second-order rutile-type to CaCl2-type phase transition in β-MnO2 at high pressure, J. Phys. Chem. Solids 56, 965 (1995).

Y. Lin, Y. Yang, H. Ma, Y. Cui, and W. L. Mao, Compressional behavior of bulk and nanorod LiMn2O4 under nonhydrostatic stress, J. Phys. Chem. C 115, 9844 (2011).

G. Herzberg and L. L. Howe, The lyman bands of molecular hydrogen, Can. J. Phys. 37, 636 (1959).

H. P. Broida and M. Peyron, Emission spectra of N2, O2, and NO molecules trapped in solid matrices, J. Chem. Phys. 32, 1068 (1960).

M. Seki, K. Kobayashi, and J. Nakahara, Optical spectra of hexagonal ice, J. Phys. Soc. Jpn. 50, 2643 (1981).

K. Uchida, K. Noda, T. Tanifuji, S. Nasu, T. Kirihara, and A. Kikuchi, Optical absorption spectra of neutron-irradiated Li2O, Phys. Status Solidi A 58, 557 (1980).

D. R. Huffman, R. L. Wild, and M. Shinnei, Optical absorption spectra of crystal field transitions in MnO, J. Chem. Phys. 50, 4092 (1969).

S. Hirai, Y. Goto, A. Wakatsuki, Y. Kamihara, M. Matoba, and W. L. Mao, Electronic structure of spin frustrated magnets: Mn3O4 spinel and postspinel, arXiv:1406.4486 [cond-mat.str-el] (2014).

Q. Javed, W. Feng-Ping, M. Y. Rafique, A. Mohammad toufiq, and M. Z. Iqbal, Canted antiferromagnetic and optical properties of nanostructures of Mn2O3 prepared by hydrothermal synthesis, Chin. Phys. B 21, 117311 (2012).

D. M. Sherman, Electronic structures of iron(III) and manganese(IV) (hydr)oxide minerals: Thermodynamics of photochemical reductive dissolution in aquatic environments, Geochim. Cosmochim. Acta 69, 3249 (2005).

P. Mort-Sánchez, A. J. Cohen, and W. Yang, Localization and delocalization errors in density functional theory and implications for band-gap prediction, Phys. Rev. Lett. 100, 146401 (2008).

I.-C. Lin, A. P. Seitsonen, I. Tavernelli, and U. Rothlisberger, Structure and dynamics of liquid water from ab
initio molecular dynamics—comparison of BLYP, PBE, and revPBE density functionals with and without van der Waals corrections, J. Chem. Theory Comput. 8, 3902 (2012).

[95] K. Forster-Tonigold and A. Groß, Dispersion corrected RPBE studies of liquid water, J. Chem. Phys. 141, 064501 (2014).

[96] T. Morawietz, A. Singraber, C. Dellago, and J. Behler, How van der Waals interactions determine the unique properties of water, PNAS 113, 8368 (2016).

[97] B. Cheng, E. A. Engel, J. Behler, C. Dellago, and M. Ceriotti, Ab initio thermodynamics of liquid and solid water, PNAS 116, 1110 (2019).