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Benchmarking DFT Functionals For Polarons In Oxides: Properties Of CeO_2

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Abstract

We examine methods for studying polarons in metal oxides with density functional theory (DFT), using the example of cerium dioxide and the standard functionals, local density approximation + U (LDA+ U), generalized gradient approximation + U (GGA+ U) in the Perdew-Burke-Ernzerhof parametrization (PBE+ U), as well as the hybrid functionals B3LYP, Heyd-Scuseria-Ernzerhof

(HSE)03, HSE06, and PBE0. We contrast the four polaron energies commonly reported in different parts of the literature: formation energy; localization/relaxation energy, Density-Of-States (DOS) level, and the polaron hopping activation barrier. Qualitatively, all these functionals predict “small” (Holstein) polarons on the scale of a single lattice site, although LDA+ U and GGA+ U are more effective than the hybrids at localizing the Ce4 f electrons. The improvements over pure LDA/GGA appear due to changes in filled Ce4 f states when using LDA/GGA+ U , but due to changes in empty Ce4 f states using the hybrids. DFT is shown to have sufficient correlation to predict both adiabatic and (approximate) diabatic hopping barriers. Overall, LDA+ U =6eV provides the best description in comparison to experiment, followed by GGA+ U =5eV. The hybrids are worse, tending to overestimate the gap and significantly underestimate the polaron hopping barriers.

1. Introduction

In recent years there has been considerable interest in the properties of metal oxides, not least due to their use in “green” technologies, such as in fuel cells,¹ three-way car exhaust catalysis² and sensors for environmental gas monitoring.³ Metal oxides can often be viewed as wide bandgap semiconductors, but the actual charge transport processes are sometimes rather complex, and this is

important for many of the applications. In some materials, an electron or hole will behave in a band-like manner, but in many others it will instead induce a local lattice distortion, breaking translational symmetry to become “self-trapped”, forming a polaron. Electron- or hole-like charge carrier transport then involves thermally activated hopping of polarons from site to site, with a measurable energy barrier to be overcome at each hop. One particularly important example of this is electrons in ceria (CeO_2), and in this paper we will use Density Functional Theory[?] (DFT) to study the structure and energetics of lone polarons in ceria, and to examine how much the predicted properties vary with choice of DFT functional.

CeO_2 has the fluorite structure, with a valence band composed primarily of $\text{O}2p$ orbitals, and a conduction band some 6 eV above composed primarily of $\text{Ce}5d$ orbitals (see Fig ??). In between lies a rather flat band of empty $\text{Ce}4f$ states, about 3 eV above the valence band edge (VBE). Any electron entering these $\text{Ce}4f$ states, by electron transfer processes at a surface or interface or through defect formation, self-traps to form a polaron. The most common such defects are oxygen vacancies, V_O . Removal of an oxygen atom leaves two extra electrons behind, which both form polarons, $\text{Ce}_{\text{Ce}}^{-1}$, but remain bound to the +2 charged vacancy, V_O^{+2} , as a neutral defect complex, $[\text{V}_\text{O}^{+2}-2\text{Ce}_{\text{Ce}}^{-1}]^0$, the low temperature structure of which has been the subject of some debate.^{???} If an energy barrier is overcome then these neutral clusters can be split up to obtain the free polarons studied here. If an electric field is placed across the sample then the polarons will hop through the Ce sublattice, carrying a current. As discussed in,[?] comparing different experimental techniques leads to a spread of possible values for the energies of these filled and empty $\text{Ce}4f$ states, as illustrated in Fig ??, but the two localized $\text{Ce}4f$ electrons at V_O in reduced CeO_{2-x} are generally found roughly 2 eV above the VBE.^{??} Conductivity studies^{?????} show that these polarons are well described by the “Small Polaron Model” of Holstein,[?] meaning that the radii of the localized charge and lattice distortion are on the order of the interatomic nearest neighbour distance. This conclusion is also consistent with scanning tunnelling microscopy images of isolated point defects,^{??} which can display a

broken symmetry at low temperature but are best described using thermal averages over localized Ce 4f states on specific Ce ions at higher temperatures.^{??} Most estimates of the $\text{Ce}4f$ polaron hopping barrier from conductivity experiments vary between 0.16 eV[?] to 0.21 eV.^{????} Note that this also forms a lower limit on the localization energy separating the filled and unfilled $\text{Ce}4f$ states.

Figure 1: Schematic diagram showing the experimental energy bands of CeO_2 . Dark shaded areas indicate the most likely positions of bands, with edge energies as indicated. Light shaded indicate the degree of uncertainty arising largely from comparison of different experimental techniques.

In DFT based studies of ceria, pure *ab initio* Local Density and Generalized Gradient Approximations (LDA and GGA) fail to describe the localisation of $\text{Ce}4f$ electrons in CeO_2 , but the LDA+ U functional^{??} with $U \approx 6$ eV and GGA+ U functional with $U \approx 5.5$ eV do achieve this.^{??} LDA+ U localises the $\text{Ce}4f$ electrons while also reproducing the experimental lattice parameter and bulk modulus to within experimental uncertainties,[?] but GGA+ $U = 5.5\text{eV}$ overestimates the lattice parameter by around 2% and underestimates the bulk modulus by around 10%.[?] Although Hartree Fock overestimates the lattice parameter and band gaps dramatically[?] (eg the $\text{O}2p \rightarrow \text{Ce}5d$ gap by 130% and the lattice parameter by 2.8%), the hybrid functionals B3LYP,[?] PBE0[?] and HSE^{??} all perform reasonably well for CeO_2 .^{?????} With their once-for-all internal parameterisations, none of the hybrids do as well as LDA+ U for bulk properties such as structure, bandgaps etc, although it has been argued that they may perform better when describing, for example, adsorbate chemistry.[?] Performance also varies amongst the hybrids, with, for example, B3LYP better than PBE0 for the electronic properties but worse for the structure.[?]

Regarding DFT simulations of the polarons themselves, Zacherle et al.[?] reported on the energetic stability of lone polarons, while Nakayama

et al.[?] reported a hopping barrier of 0.18 eV from GGA+ U , and Su et al.[?] found the same value for polarons bound to V_O^{+2} on the (111) surface. Plata et al. reported hopping barrier estimates of 0.4 eV in the bulk[?] and a range from 0.3-0.5 eV for some barriers near to the (111) surface[?] based primarily on unrestricted Hartree-Fock (HF) calculations. However, the detailed nature of the polaron, and the way in which predicted properties vary with both functional and supercell (periodic boundary conditions), have not yet been assessed in the literature. Furthermore, different authors quote different types of energies. Some use primarily Density Of States (DOS) plots, some use relaxation/localization energies, and others use defect formation energies, making comparison between studies hard.

Despite their importance, the characterization of polarons in metal oxides, their effective size, energetics and mobility, therefore remains challenging and under-explored, partly due to the difficulty in studying trapped electrons and their mobility using computational techniques. We will address that by examining and comparing protocols for reliable characterization of polarons using DFT methods, as well as undertaking a detailed, consistent study of the properties of polarons in CeO_2 , in which we examine energetics, degree of localisation, migration barriers and energy levels. We analyse the differences in predictions between LDA+ U , GGA+ U (specifically, PBE+ U) and the hybrids B3LYP, PBE0, HSE06 and HSE03, and hence we compare the alternative methods of calculating polaron stability energetics. By comparing with experimental data, we analyse the differences in performance between the different functionals and attempt to identify which produces the most consistent description of the polaron properties. The next section will summarize the technical details and discuss the definitions of the various reported polaron energies, and the links between them. We will examine the predicted values of those energies for polarons in ceria in section 3, first using LDA+ U and GGA+ U , then using hybrids. We then discuss the effective size of the polarons in section 4, and the diabatic and adiabatic hopping barriers in section 5. In section 6, we use the LDA+ U functional with $U=6$ eV together with finite size scaling to predict the properties of lone

polarons in ceria and compare them to experiment. In section 7, we conclude.

2. Methods and energies

2.1 Technical details

We use plane-wave *ab initio* DFT together with the Projector Augmented Wave method[?] (PAW) within the VASP code.[?] We treat $\text{O}2s^22p^4$ and $\text{Ce}4f^15s^25p^65d^16s^2$ as valence, with a planewave cutoff of 300 eV. Tests indicate that for this study, increasing the planewave cutoff to 500 eV makes only rather small changes. The valence band and empty $\text{Ce}4f$ band edges shift by 0.001 eV and 0.004 eV using LDA+ U and by 0.001 eV and 0.009 eV for HSE06. Increasing the planewave cutoff to 500 eV without further relaxation shifts the polaron energies, E_{DOS} , $E_{\text{Localization}}$, and E_{Transfer} , (see definitions below,) by 0.004 eV, 0.011 eV and 0.010 eV respectively for LDA+ U and by 0.019 eV, 0.010 eV and 0.010 eV respectively for HSE06. In the case of LDA+ U , re-doing the entire relaxation with a 500eV planewave cutoff alters the nearest neighbour distances by only 0.00018 Å, which is 0.2% of the total relaxation when the polaron forms, and alters the energies by 0.019 eV, 0.017 eV and 0.018 eV compared to the 300 eV relaxation. Re-calculating the polaron hopping barrier using LDA+ U with a 500eV planewave cutoff shifts the barrier energies E_{Diabatic} and $E_{\text{Adiabatic}}$, (again, see below for definitions,) by 0.002 eV and 0.001 eV respectively. All of these shifts are small compared to the differences in energies, degree of localization and structure coming from changing between different functionals.

Most results will be for a 96 atom simple cubic supercell, which is a $2 \times 2 \times 2$ multiple of the 12 atom crystallographic cell, itself containing 4 primitive unit cells. With that supercell, k-point integration is over a $4 \times 4 \times 4$ Monkhorst-Pack[?] grid for LDA+ U and GGA+ U calculations (which use the PBE[?] form of GGA and the + U form proposed by Dudarev et al.[?]) and over a $2 \times 2 \times 2$ grid for calculations using hybrid functionals. For LDA+ U , this reduction in k-point grid changes the relaxation energy, $E_{\text{Relaxation}}$, (see below,) by 0.014 eV.

Comparison results in 12 atom ($1 \times 1 \times 1$) and 324 atom ($3 \times 3 \times 3$) supercells use respectively a $4 \times 4 \times 4$ k -point grid and the single $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ special point; ie an O_h symmetry-enforced $2 \times 2 \times 2$ Monkhorst-Pack grid. Polarons are formed by adding an extra electron to the supercell, together with a uniform compensating background charge, and then allowing the system to relax.

2.2 Polaron Energy Definitions

In the literature, there are three different calculated energies used to estimate the position of the filled $Ce4f$ states within the $O2p \rightarrow Ce4f$ bandgap, but they are not normally used and compared in the same work, and we are not aware of their definitions being set out and compared elsewhere. However, the limitations of DFT with specific functionals may affect these three energies differently, so comparing them provides a more complete picture of the properties of the polarons themselves and the limitations of the functionals.

1. Density of States (DOS) level:

The simplest energy to use is the DFT calculated DOS for the supercell containing the relaxed polaron (often reported only via a DOS plot). This should be equivalent to the experimental picture shown in Fig ??, with a filled $Ce4f$ state at an energy E_{DOS} above the VBE, ϵ_{VBE} . This identifies the polaron state within a single particle approximation, ignoring the facts that i) since Koopmans' theorem does not hold, single particle Kohn-Sham energies within DFT do not formally correspond to single particle DOS energies, ii) no tractable DFT functional treats all bandgaps correctly, and iii) the presence of a polaron within the finite supercell will locally distort the bands and the empty $Ce4f$ states.

2: Relaxation energy:

Calculating the total energy of a pure, stoichiometric ceria supercell, with all ions at equilibrium positions and no relaxation, leaves all $Ce4f$ states empty and delocalized, forming a narrow band ~ 1 eV wide. If one extra electron is added, it enters the lowest available Kohn-Sham state at the bottom of that delocalized $Ce4f$ band. If no further ionic relaxation or translational symmetry break-

ing is permitted then the electron remains in that delocalized $Ce4f$ state, and we can evaluate the total energy $\mathcal{E}^{Total}(\text{Delocalized } Ce4f)$ of that state. If we then allow lattice relaxation, and remove any symmetry restrictions, a polaron forms with the electron in a localized $Ce4f$ state centred on one particular Ce ion, and we can again evaluate the total energy $\mathcal{E}^{Total}(Ce4f \text{ polaron})$. The relaxation energy (sometimes called the localization or stabilization energy) is then defined as:

$$E_{Relaxation} = \mathcal{E}^{Total}(\text{Delocalized } Ce4f) - \mathcal{E}^{Total}(Ce4f \text{ polaron}) \quad (1)$$

This is often used to identify the energy of the polaron state relative to the empty $Ce4f$ band, meaning that it can be located on Fig ?? as lying energy $E_{Relaxation}$ below the unperturbed empty $Ce4f$ band, at least in the large supercell limit. In other words, it is located at energy

$$E_{Localization} = \epsilon_{Ce4f}^0(\text{Empty}) - E_{Relaxation} \quad (2)$$

above the VBE, where $\epsilon_{Ce4f}^0(\text{Empty})$ is the bottom of the empty $Ce4f$ band.

3: Defect transfer level:

Alternatively, we can identify the energy of the polaron relative to the VBE directly by treating it as if it were a more standard charged point defect in a semiconductor or insulator (see method reviews??), calculating its “defect formation energy” $E_{Formation}$. This is the energy cost of creating a particular defect in a particular charge state, at equilibrium with suitable charge and atom reservoirs within a grand canonical scheme, albeit normally evaluated at 0 K. It is defined?? as

$$E_{Formation} = \mathcal{E}^{Total}(\text{defect}^q) - \mathcal{E}^{Total}(\text{clean}) - \sum_i \mu_i n_i + q (\epsilon_{VBE} + \epsilon_{Fermi}) \quad (3)$$

where $\mathcal{E}^{Total}(\text{defect}^q)$ and $\mathcal{E}^{Total}(\text{clean})$ are the total energy of the supercell with and without the defect, calculated using the same values of planewave cutoff, k -point grid, etc. The energy for the charge reservoir is the Fermi level, ϵ_{Fermi} , which is measured relative to ϵ_{VBE} and is usually

treated as a free parameter. (In many materials, doping techniques allow ϵ_{Fermi} to be deliberately placed almost anywhere within the bandgap.) ϵ_{VBE} is found in a clean bulk supercell, but adjusted to align the local potentials in the defect and bulk supercells.⁷ (We use the average potential over all of the cell except the inner $\frac{1}{8}$ of the cell nearest the polaron.) The defect is created by adding n_i ions of chemical potential μ_i . However, in the case of a polaron, no ions have been added or removed, and $q = -1$ so we have simply:

$$E_{\text{Formation}} = \mathcal{E}^{\text{Total}}(\text{Ce}4f \text{ polaron}) - \mathcal{E}^{\text{Total}}(\text{clean}) - (\epsilon_{\text{VBE}} + \epsilon_{\text{Fermi}}) \quad (4)$$

Since $q = -1$, $E_{\text{Formation}}$ has a maximum at the VBE, and decreases linearly with ϵ_{Fermi} . At a particular value of ϵ_{Fermi} , called the transfer level, E_{Transfer} , the value of $E_{\text{Formation}}$ becomes negative, meaning that polarons form spontaneously at or above this point in the band gap. (Having such a value of ϵ_{Fermi} implies the presence of a source of electrons elsewhere in the grand canonical system.) Hence the value $\epsilon_{\text{Fermi}} = E_{\text{Transfer}}$ at which $E_{\text{Formation}}$ becomes zero corresponds to the location in the bandgap of the filled Ce4f states, identifying the polaron state relative to the VBE. Hence

$$E_{\text{Transfer}} = \mathcal{E}^{\text{Total}}(\text{Ce}4f \text{ polaron}) - \mathcal{E}^{\text{Total}}(\text{clean}) - \epsilon_{\text{VBE}} \quad (5)$$

Comparing the three energies:

There are therefore three different measures in use to describe the energetics of polaron formation. With a hypothetical exact functional, E_{Transfer} would be $\approx E_{\text{Localization}}$. (I.E. $E_{\text{Transfer}} + E_{\text{Relaxation}} \approx$ the O2p $\rightarrow$ Ce4f(empty) bandgap). The nature of E_{DOS} is slightly different since it is a single particle energy (coming from individual Kohn-Sham levels), while E_{Transfer} and $E_{\text{Relaxation}}$ are derived from total energies, so include more many particle effects. Since in practice we have neither a perfect functional, nor Koopmans' theorem, the three energies all provide different estimates of the position of the filled Ce4f states, using different reference states. The *differences* between the three measures give some indication of the degree of internal consistency in the

polaron descriptions obtained using different functionals and also of the relative importance of many particle effects.

3. Where is the polaron state within the bandgap?

3.1 Energetics using LDA+U and GGA+U.

We showed previously⁷ that for LDA+U the degree of localization follows a rough $\cap$ shape as a function of U , being small for $U \leq 5$ eV, and falling again for $U \geq 7$ eV, with an onset around $U \approx 3$ eV and a maximum around $U \approx 6$ eV. The behaviour of GGA+U is similar, with a maximum around $U \approx 5$ eV. The onset of localization can also be seen in Fig ??, which shows the variation with U of E_{DOS} , $E_{\text{Localization}}$, E_{Transfer} and the band edges, for a) LDA+U and b) GGA+U. The filled Ce4f polaron state has split off from the empty band by LDA+U ≈ 4 eV or GGA+U ≈ 3 eV. E_{DOS} then descends roughly linearly with U , falling 2.1 eV to reach the valence band at $U \simeq 10$ eV. $E_{\text{Formation}}$ and $E_{\text{Localization}}$ are very similar to one another, splitting off at the same point as E_{DOS} , but descending more slowly, being consistent with E_{DOS} only over a limited range of U values. This linear dependence contrasts with that of the degree of spatial localization of the polaronic charge within the supercell, which has a flat plateau around the U value that gives the best description of localized polarons.⁷ Hence, lowering or raising the value of U by only 1 eV changes the predicted E_{DOS} value by $\sim 25\%$, but changes the degree of spatial localization by only $\sim 0.5\%$. This lack of a plateau near the optimal U value is a potential pitfall, since it means that some predicted polaron properties are much more dependent on the fine-tuning of the functional than others. (Similar behaviour was previously⁷ found for both the formation energy and degree of localization of neutral vacancy-bipolaron complexes, $[V_O^{+2} - 2Ce_{Ce}^{-1}]^0$.)

Note that while changing U from 4 to 10 eV shifts the filled Ce4f state by 2.1 eV (here considering E_{DOS}), the effect on the *empty* states is much

Figure 2: Bands in ceria with one filled $Ce4f$ state, as a function of: (a) U for LDA+ U , (b) U for GGA+ U , and (c) μ for HSE-type functionals. All are plotted with pure LDA/PBE on the left. For the HSE-type functionals the values $\mu = 0, 0.2, 0.3 \text{ \AA}^{-1}$ and the limit $\mu \rightarrow \infty \text{ \AA}^{-1}$ correspond to PBE0, HSE06, HSE03 and pure PBE respectively. The empty $Ce4f$ and $Ce5d$ states are taken from DOS. For the filled $Ce4f$ state, three energies are shown: E_{DOS} ($\circ$, dotted, red, reported previously[?] for LDA+ U and GGA+ U), $E_{Localization}$ (+, solid, green) and $E_{Transfer}$ ($\times$, dashed, blue). All energies are relative to the VBE.

milder, with the $Ce4f$ (empty) states rising by only 0.7 eV and the $Ce5d$ states falling by 0.4 eV over the same range of U values. In other words, the improvement in the description of the polarons obtained from LDA+ U and GGA+ U is due primarily to the effect U has on the *filled* $Ce4f$ states.[?]

It has been suggested that an additional “ U ” should be applied to the oxygen $O2p$ orbitals (see[?] for example). We have therefore tested forming a polaron using GGA+ $U_{Ce4f} + U_{O2p}$ with $U_{Ce4f} = 5\text{ eV}$ and $U_{O2p} = 5\text{ eV}$. The original physical justification for adding a U value to the $Ce4f$ states was that they are highly localised, so local Coulomb, correlation and exchange effects are particularly strong. $O2p$ orbitals are not nearly so localised, so in principle the correlation effects etc. should be milder at $O2p$ than at $Ce4f$, making a smaller value of U_{O2p} more appropriate. We have therefore also tested LDA+ $U_{Ce4f} + U_{O2p}$ with $U_{Ce4f} = 6\text{ eV}$ and $U_{O2p} = 2\text{ eV}$. In the case of LDA+ $U_{Ce4f} + U_{O2p}$ we find no significant improvements. For bulk properties the bandgap widens by only 0.03 eV and the lattice parameter is reduced slightly to $5.40 \text{ \AA}$, though it remains in agreement with experiment.[?] The polaron energies shift downwards only very slightly (to $E_{DOS} = 1.59 \text{ eV}$, $E_{Localization} = 1.87 \text{ eV}$ and $E_{Transfer} = 1.90 \text{ eV}$). For GGA+ $U_{Ce4f} + U_{O2p}$ with the larger value of U_{O2p} we do find more improvement. The bandgap widens to match that obtained using LDA+ U (without U_{O2p}), while the lattice parameter shrinks, though to a still over-estimated $5.47 \text{ \AA}$. The polaron energies shift upwards a little, to $E_{DOS} = 2.06 \text{ eV}$, $E_{Localization} = 2.05 \text{ eV}$ and $E_{Transfer} = 2.08 \text{ eV}$, which is slightly higher than the values obtained using LDA+ U . The overall picture is that for polarons in ceria, GGA+ $U_{Ce4f} + U_{O2p}$ is indeed an improvement on GGA+ U_{Ce4f} , but is still slightly worse compared to experiment than LDA+ U_{Ce4f} .

3.2 Energetics using hybrids.

In Fig ??, we show E_{DOS} , $E_{Localization}$ and $E_{Transfer}$ calculated in the 96 atom supercell with LDA+ $U=6 \text{ eV}$, PBE+ $U=5 \text{ eV}$, and a range of different hybrid functionals, compared to the experimental values. None of the hybrids performs as well as LDA+ U and GGA+ U , as evident also from some previous studies.^{?????} The

Figure 3: Comparison of the predicted and experimental positions of filled and empty $\text{Ce}4f$ states, relative to the valence band edge (VBE). Filled (polaronic) levels are shown as calculated using E_{DOS} (dotted, red), $E_{Localization}$ (solid, green), and $E_{Transfer}$ (dashed, blue). Empty $\text{Ce}4f$ states are shown starting from the lower limit solid (maroon) line and the shaded region above it. Results calculated in the 96 atom supercell.

$\text{O}_{2p} \rightarrow \text{Ce}_{4f}(\text{Empty})$ gap is always overestimated, though HSE03, HSE06 and B3LYP only overestimate by roughly as much as LDA+U and GGA+U underestimate it. The overestimation with PBE0 is more significant. Note that Freysoldt corrections[?] to $E_{Transfer}$ and $E_{Localization}$ are not shown here in order to ease comparison with E_{DOS} for which the corrections are hard to apply directly. However the Freysoldt corrections are all small: +0.05 eV for B3LYP and PBE0, +0.07 eV for HSE03, HSE06 and GGA+U, and +0.06 eV for LDA+U.

Du *et al.*[?] showed in a recent publication that the problem of the overestimated gap may be alleviated either by reducing the amount of exact exchange in HSE to 15%, (rather than the default value of 25%,) or by increasing the screening, although the latter was not fully explored in their work. We will discuss this further in the next subsection.

HSE03 and HSE06 both produce reasonably self-consistent sets of energies, but they are much too close to the overestimated $\text{Ce}_{4f}(\text{Empty})$ band edge. The two hybrid functional used here which do *not* include screening of the Hartree-Fock terms, namely B3LYP and PBE0, both produce qualitatively reasonable sets of energies, but are less mutually self-consistent, being spread over about 0.5-0.6 eV.

Note that it is also possible to plot the movement of all of the bands with respect to the electrostatic potential, rather than relative to the valence band edge, as done in Ref.[?] If one does that, then going from HSE06 to PBE0 produces a 0.4 eV shift

upwards for all empty states and downward for all filled states, in agreement with Ref.[?] and consistent with the expect general behaviour derived by Komsa *et al.*[?]

Overall, the results produced by the hybrids are qualitatively reasonable, but quantitatively they are in poorer agreement with experiment than LDA+U and GGA+U, unless, as is apparent from Ref.[?] either the amount of exact exchange is modified, or the amount of screening is modified.

3.3 Comparing hybrids with LDA/GGA+U.

Much of the variation amongst the hybrids, and the significant differences between them and LDA+U/GGA+U, can be understood by contrasting Fig ?? part c) with parts a) and b). The HSE functional contains a screening range separation parameter μ , which is related to an inverse distance. Below this cut-off distance (short range) HF exchange is used, while above it (long range) PBE exchange is used. Hence choosing $\mu = 0 \text{ \AA}^{-1}$ gives the PBE0 functional, $\mu = 0.2 \text{ \AA}^{-1}$ gives HSE06 and $\mu = 0.3 \text{ \AA}^{-1}$ gives HSE03, and the limit $\mu \rightarrow \infty \text{ \AA}^{-1}$ recovers pure PBE. We may therefore use the μ parameter to track from PBE to PBE0 via HSE03 and HSE06. One could also track from PBE to HSE06 by varying the amount of exact exchange, α , for a fixed value of $\mu = 0.2$. This was done recently by Du *et al.*,[?] who plotted the $\text{O}_{2p} \rightarrow \text{Ce}_{4f}(\text{Empty})$, $\text{O}_{2p} \rightarrow \text{Ce}_{5d}$ band gaps of bulk ceria as well as the E_{DOS} value for the localized $\text{Ce}4f$ electrons associated with the neu-

tral vacancy-bipolaron complex $[V_O^{+2}-2Ce_{Ce}^{-1}]^0$. They plotted two series, one from PBE to HSE06 using α values in a range from 0 to 0.25 and one from PBE0 to HSE03 using μ values in a range from 0.0 to 0.3 $\text{\AA}^{-1}$. Examining their data, it is clear that the two parameters, α and μ , have an inverse relation in terms of their effect on the $O_{2p} \rightarrow Ce_{4f}(\text{Empty})$ gap and the E_{DOS} value. For example, using HSE06 with $\mu = 0.2 \text{ \AA}^{-1}$ and $\alpha = 0.2$ gives the same results to within 1.5% as using HSE03 with $\mu = 0.3 \text{ \AA}^{-1}$ and $\alpha = 0.25$. The screening therefore acts primarily to reduce the effective amount of exact exchange included in the functional, at least in this case. Hence either tracking should provide similar understanding, so we opt to present our results using the μ tracking since it allows us to compare the HSE03, HSE06 and PBE0 all within the same graph.

Fig ?? c) shows the band edges, $E_{Transfer}$, $E_{Localization}$ and E_{DOS} as a function of μ (shown right to left to allow comparison with parts a) and b)). Very clearly, the screening range is of great importance to the description of localized Ce_{4f} charges using the hybrids, with polaron localization only really described for $\mu \leq 0.5 \text{ \AA}^{-1}$. However, it should be noted that once the $Ce_{4f}(\text{filled})$ state has localized and split off from the $Ce_{4f}(\text{empty})$ band, none of the three estimates $E_{Transfer}$, E_{DOS} or $E_{Localization}$ vary greatly with μ . Instead, it is largely the empty states which shift with μ . In other words, if we extend LDA or GGA using the LDA+ U approach, the improvements in the description of Ce_{4f} polarons occur due to the effect of the + U on the filled Ce_{4f} states (they move downwards), but in contrast, if we extend LDA or GGA by including some Hartree-Fock exchange, it could be argued that the improvements occur due to the effect of the Hartree-Fock-like terms on the *empty* states (they move upwards). As a result, while either approach may produce qualitatively reasonable results, their detailed predictions for the properties of polarons and other features of ceria are likely to contain some differences, so the choice of approach still needs to be taken with care.

4. How large are the polarons?

We previously reported[?] isocharge surfaces for the Ce_{4f} polarons containing different percentages of the total charge of the polaron for a range of functionals. In Fig ??a) we show the volume percentage of the supercell contained within the 90%, 95% and 99% isocharge surfaces. I.E. we show how much of the supercell must be summed over in order to capture 90%, 95% and 99% of the polaron charge. If the charge of the polaron were completely localised onto a single Ce ion then the 100% isocharge surface would fill roughly 1% of the supercell. For LDA+ U and GGA+ U over 90% of the polaron charge is contained within a single lattice site, in reasonably good agreement with the experimental evidence, though there remains a thin “tail” of charge spreading out beyond the nearest neighbour distance. Nevertheless, the 99% of the polaron charge is contained within 6% of the volume of the supercell. The degree of charge localization achieved by the hybrids is significantly less, indicating that they do not perform as well, though they do remain within the “small polaron” regime. A similar observation for localized Ce_{4f} electrons within neutral vacancy-bipolaron complexes $[V_O^{+2}-2Ce_{Ce}^{-1}]^0$ was made in Ref.[?] where the spatial extent of the spin density was analysed.

The degree of structural localization of the polaron is rather more uniform between the different functionals as shown in Fig ??b), which gives the percentage change in neighbour distances compared to the clean lattice. Clearly, the presence of the polaron has almost no effect on surrounding Ce ions, but surrounding O ions are all moved outwards; by around 3% for the first shell, falling to 0.25%, 0.06% and 0.01% in surrounding shells. Structurally, the polaron is again very localized, and all functionals give more or less the same degree of localization.

5. Polaron migration barriers.

Migration barriers for polarons in metal oxides tend to be considered within the context of Marcus theory,[?] as outlined, for example, by Deskins and Dupuis.[?] The key points are illustrated in Fig

Figure 4: Comparison of the degree of localization achieved for the polaron using various functionals in the 96 atom supercell. a) Charge localization: The percentage of the total *volume* of the supercell filled by isocharge surfaces which contain 90%, 95% and 99% of the $\text{Ce}4f$ polaron charge. Perfect localization onto a single Ce site would mean that the 100% isocharge surface filled only about 1% of the supercell. b) Structural localization, shown as the percentage change in the distance from the polaron centre to surrounding shells of neighbours.

Figure 5: Schematic diagram illustrating the Marcus theory approach to polaron hopping. The polaron moves from a parabolic potential energy surface for an initial state at site 1, to a parabolic potential energy surface for a final state at site 2. The crossing point of the two surfaces gives an estimate of the diabatic barrier. Quantum tunnelling is permitted by electronic coupling strength V_{12} , leading to an estimate of the lower adiabatic barrier.

?? Roughly, the polaron is treated as being in an initial state centred on site 1, and moving to a final state centred on site 2. In both, the potential well is considered to be parabolic. The crossing point of the two parabolas gives the diabatic barrier height, $E_{Diabatic}$, in which the polaron remains on one of the two parabolic Born-Oppenheimer surfaces (the lower one) at all stages. Polaron hopping over the diabatic barrier then corresponds to an antiphase breathing mode, inwards on site 1 and outwards on site 2. However, there will also be a degree of overlap between the wavefunction for a polaron at site 1 and the wavefunction for a polaron on site 2, which can be characterised by the electronic coupling strength V_{12} . This allows quantum tunnelling of the polaron under the diabatic barrier, leading to the adiabatic barrier, $E_{Adiabatic}$, which is V_{12} lower in energy.

In practice, the general approach^{???} is to estimate $E_{Diabatic}$ using standard electronic structure methods, (such as DFT,) by calculating the energy of a series of structures linearly interpolated between a fully relaxed polaron at site 1, and one at site 2. Directly evaluating V_{12} involves calculating the difference between ground and excited states in which the polaron is located at 1, but with relaxed structures corresponding to the polaron being at 1 or at 2, respectively. This can be done using constrained DFT,^{???} although this is

not formally supported within VASP and similar planewave codes at present. One alternative is to calculate V_{12} *a posteriori* using a separate two centre restricted configuration interaction (R-CI) calculation, performed on the basis of the single states either side of the barrier. Plata et al.² attempted to do this using hybrid functionals, but had computational difficulties near the barrier itself, so instead estimated $E_{Diabatic}$ using unrestricted HF, obtaining the value 0.48 eV. (They then estimated V_{12} , but *not* $E_{Adiabatic}$ itself using several hybrid functionals, obtaining 0.085 eV for PBE0, 0.083 eV for B3LYP, 0.068 eV for HSE06, and 0.088 eV for M06. They then concluded that a likely value is $E_{Adiabatic} \approx 0.4$ eV, roughly twice the common experimental value. We note that unrestricted HF also overestimates the bandgap by a similar factor ($\times 2.3$) though this may not be related.

Alternatively, one can attempt to calculate $E_{Adiabatic}$ directly, by using DFT to find the ground states of restricted structures along the hopping path.²² Nakayama et al.² used this approach to calculate the ceria polaron hopping barrier directly using GGA+ $U=5$ eV, obtaining $E_{Adiabatic} = 0.18$ eV. The limitation here is in the accuracy of the description of the (restricted) state at the saddle point. The HF + CI approach builds in correlation directly, albeit not necessarily to high levels in CI. Whilst DFT does not have complete correlation, it does have *some*, even at LDA level, and has more with more advanced functionals. If we have a charge density split equally between two sites, then we will have as much correlation as the DFT functional in question is able to provide *at both sites*. In other words, if the degree of correlation included in the functional in question is sufficient, then we *should* be able to estimate the adiabatic barriers.

In Fig ??, we show barriers obtained using various functionals, with barrier heights listed in Table ?. In Fig ??a), we show the results of a linear interpolation calculation (circular symbols) using LDA+ $U=6$ eV. The solid (blue) curves are pure parabolas, one at the initial site, one at the final site, and are fitted to the first/last 5 data points. (Higher order polynomials have been tried but the improvement in the fit is negligible, with, for example, a Chi-squared test improving by only 4%, and the predicted barrier shifting by less than the

Figure 6: Linearly interpolated barriers calculated using a) LDA+ U , b) HSE06 c) GGA+ U , d) HSE03, and e) PBE0. Calculated image energies are shown as open black circles. Small blue filled circles indicate points used to extrapolate diabatic barriers, $E_{Diabatic}$, (solid blue lines) and red $\times$ indicate points used to extrapolate adiabatic barriers, $E_{Adiabatic}$, (solid red lines). Dashed/dotted lines are extrapolations using one more/less data point (or additional pairs of data points for adiabatic barriers) to assess reliability of solid line extrapolations. Note: for LDA+ U , GGA+ U the adiabatic barrier comes from the converged central data point, so red lines are shown for illustration purposes only.

Table 1: Adiabatic ($E_{Adiabatic}$) and Diabatic ($E_{Diabatic}$) polaron hopping barriers for different functionals, estimated from Fig ??, and the electronic coupling strength V_{12} obtained as the difference between them. Error bars indicate reliability of extrapolations, but for adiabatic barriers this is less than ± 0.001 in all cases.

Functional	$E_{Adiabatic}$	$E_{Diabatic}$	V_{12}	Literature
LDA+ U	0.197	0.222 ± 0.008	0.025 ± 0.008	
LDA+ $U+U$	0.207	0.221 ± 0.009	0.014 ± 0.009	
GGA+ U	0.109	0.22 ± 0.05	0.11 ± 0.05	Adiabatic: 0.18 ^a
GGA+ $U+U$	0.090	0.19 ± 0.05	0.10 ± 0.05	
HSE03	0.027	0.09 ± 0.02	0.06 ± 0.02	
HSE06	0.051	0.15 ± 0.02	0.10 ± 0.02	V_{12} : 0.068 ^b
PBE0	0.062	0.26 ± 0.10	0.20 ± 0.10	V_{12} : 0.085 ^b
HF				Diabatic: 0.48 ^b

^a From ? ^c From ?

error bar shown in Table ??.) The two parabolas cross at 0.224 eV, providing an LDA+ U estimate of $E_{Diabatic}$. A rough measure of the uncertainty in this extrapolation can be obtained as ± 0.007 eV by comparing extrapolations using the first/last 4 or 6 data points. The directly calculated mid-point, meanwhile, is lower, at 0.197 eV, and provides an estimate of $E_{Adiabatic}$. If we attempt to calculate it using a nudged elastic band (NEB[?]) calculation starting from those linearly interpolated structures we get the same value, with intermediate images simply sliding down the parabolas. This indicates that the process taking place at the barrier is indeed an essentially electronic one, not ionic. The difference ($E_{Diabatic} - E_{Adiabatic}$) = 0.027 eV provides an indirect estimate of V_{12} .

Fig ??b) shows the barrier calculated using HSE06. As with Plata et al.,[?] we are unable to get the centre point to converge using this functional. However, in our case all the other points do converge. Near the initial and final states they again fit well to pure parabolas. (Adding a higher order term to the fit only improves a Chi-squared test by $\sim 0.16\%$, with the fitted coefficient of the higher order terms at least 0.004 times smaller than the quadratic term.) If we extrapolate the pure parabolas we estimate that $E_{Diabatic} = 0.15 \pm 0.02$ eV, using the first/last 4 data points for the extrapolation, and comparing to using 3 or 5 point to estimate the extrapolation uncertainty. Near but not at the un-

converged middle point, the images *do* converge, to values below the parabola. Indeed, they become flat towards the middle allowing us to estimate $E_{Adiabatic} = 0.0512$ eV by fitting another (red) parabola to the middle 6 data points. Comparison to fitting to the middle 4 or 8 points indicates that the uncertainty in the extrapolation this time is 0.0002 eV - which is less than the uncertainty from the truncation of either basis set or k -point integration. Alternatively, adding higher order terms to the parabolic fit shifts $E_{Adiabatic}$ by ~ 0.0001 eV. The difference ($E_{Diabatic} - E_{Adiabatic}$) again gives us an indirect estimate of V_{12} of 0.10 ± 0.02 eV which is close to the value of 0.068 eV obtained by Plata et al.[?] using restricted CI.

Fig ??c-e) show equivalent results for the functionals GGA+ U , HSE03 and PBE0, extrapolated as above using the data points indicated in the figure. With GGA+ U , we find a similar value for $E_{Diabatic}$ to the that from LDA+ U , though the $E_{Adiabatic}$ value is somewhat lower with GGA+ U than with LDA+ U . We do not reproduce Nakayama et al.'s value,[?] which was reported as $E_{Diabatic}$ but is actually rather closer to our $E_{Adiabatic}$ value. The reason for the difference is not clear. Regarding the hybrids, the general trend is that the adiabatic barriers are much smaller (0.03-0.06 eV) than those obtained from LDA+ U and GGA+ U (0.2 and 0.1 eV). The latter are of the same order as the experimental values,

the hybrid barriers are not. Indeed, for HSE03 and HSE06 even the higher diabatic barrier is significantly less than the experimental barriers, so for ceria polaron hopping barriers the hybrids actually perform rather poorly.

We note that the barriers computed using the hybrid functionals become smaller with increasing screening parameter μ . It is plausible that the under-estimation may be corrected either by further reducing the screening, or by increasing the amount of Hartree-Fock exchange included, (or a combination of both). However, either of these approaches would further worsen the agreement with experiment for the band energies themselves.

Meanwhile, all the values of V_{12} obtained are of a similar magnitude to those found by Plata et al.,[?] though with too large an uncertainty for detailed comparison. Indeed, these uncertainties mean that this is certainly not a method of choice for V_{12} or the diabatic barriers, but it does at least give a rough estimate when other methods are not available, as is currently the case with standard VASP. It is also worth noting that almost all the extrapolation uncertainty lies in the diabatic barrier, not in the adiabatic barrier which is the more relevant one when comparing to most conductivity experiments, for example.

Finally, Table ?? also lists the barriers obtained using $\text{GGA}+U_{\text{Ce}4f}+U_{\text{O}2p}$, and $\text{LDA}+U_{\text{Ce}4f}+U_{\text{O}2p}$ (both parameterised as before). The effects of $+U_{\text{O}2p}$ are very modest in both cases, slightly worsening the $\text{GGA}+U_{\text{Ce}4f}+U_{\text{O}2p}$ result compared to experiment, and keeping it in reasonable agreement with experiment for $\text{LDA}+U_{\text{Ce}4f}+U_{\text{O}2p}$.

6. Properties of polarons in the low density limit.

All of our calculations thus far have used the 96 atom supercell, corresponding to an infinite 3 dimensional ordered array of polarons, of concentration $\sim 3\%$. There will therefore be residual errors due to the supercell approximation, with potentially significant contributions owing to: incomplete relaxation due to the small size of the supercell, electrostatic and elastic defect-defect image interactions, and quantum mechanical overlap between the localized levels on the defect and

Figure 7: Polaron energies versus inverse supercell size: (a) Relaxation energy $E_{\text{Relaxation}}$, (b) Transfer Level E_{Transfer} , (c) DOS level E_{DOS} , and (d) Adiabatic polaron bulk migration barrier height. Blue + symbols are calculated data points, with no corrections. Green $\times$ symbols use Freysoldt corrections to the total energies of the localized polaron. Solid lines are fits to equation ?? with $n=3$. The scaled values are shown with error bars to the left of the y-axis. The error bars are obtained by comparing to fits using all three supercells to equation ?? with $n=2$ and 4, and to linear fits using the 96 and 324 atom supercell results only. Horizontal (green) lines and vertical (green) arrows are guides to the eye.

its periodic images. (See reviews,^{2,3,4,5} for example). These can be treated using finite size scaling,² or using correction schemes, particularly that developed by Freysoldt et al.² (Other schemes have been presented, notably that of Makov and Payne,^{2,6} but are generally not sufficiently reliable.^{2,3,4,5,7})

Finite size scaling can be done by repeating the same defect calculation to obtain, for example, a series of different formation energies $E_{\text{Formation}}(L)$ in supercells of characteristic linear dimension L . The finite size scaled (corrected) formation energy, $E_{\text{Formation}}^{L \rightarrow \infty}$, then is obtained by fitting those energies using the scaling formula:

$$E_{\text{Formation}}(L) = E_{\text{Formation}}^{L \rightarrow \infty} + a_1 L^{-1} + a_n L^{-n} \quad (6)$$

where a_1 , a_n and $E_{\text{Formation}}^{L \rightarrow \infty}$ are treated as fitting parameters. $E_{\text{Formation}}^{L \rightarrow \infty}$ is the formation energy of the polaron in an infinite supercell, or equivalently a lone or isolated polaron in the low density limit. Generally, $n = 3$ is most accurate,² i.e. the errors scale with the linear dimensions and with the volume of the supercell. Unfortunately, for CeO_2 our computational resources only permit us to calculate $E_{\text{Formation}}(L)$ in supercells of 12, 96 and 324 atoms, as shown in Fig ??, for $E_{\text{Relaxation}}$ in part a), for E_{Transfer} in part b) and for E_{DOS} in part c). Using equation ?? with $n = 3$ to extrapolate the calculated values we obtain a lone polaron relaxation energy of $E_{\text{Relaxation}} = 0.42 \pm 0.01$ eV. This error estimate for the scaling takes account of the results of scaling with $n = 2, 4$ and the linear scaling from the 96 and 324 atom supercells. The bottom of the Ce4f empty band lies at 2.46 eV (independent of supercell size), giving $E_{\text{Localization}}^{L \rightarrow \infty} = 2.04 \pm 0.01$ eV. Similarly, scaling $E_{\text{Transfer}}^{L \rightarrow \infty}$ gives 2.00 ± 0.03 eV. Finally, the scaling of E_{DOS} gives 1.68 ± 0.02 eV. As shown in Fig ??, these three scaled values for the energy of a lone polaron are reasonably consistent with one-another, and are all in good keeping with experiment, indeed closer even than the unscaled 96 atom supercell LDA+U=6eV values.

It should be noted, however, that the effects of supercell size on these energies are not especially great - compared to the scaled lone polaron values, the values of $E_{\text{Relaxation}}$, E_{Transfer} and E_{DOS} obtained in the 96 atom supercell are only wrong

by 0.21, 0.13 and 0.07 eV respectively (10%, 7% and 4%), which is much less than the errors for charged point defects in other materials (e.g.²) which are sometimes on the order of several eV.

In Fig ??a) and b), we also show the effects of using the correction scheme of Freysoldt et al.² for the case of polarons in bulk ceria. For both $E_{\text{Relaxation}}$ and E_{Transfer} , in all three supercells, we find that the corrections help, but do not actually recover the scaled values for a lone polaron, correcting only about $\frac{1}{3} \rightarrow \frac{1}{2}$ of the error. This scheme only corrects the effects of spurious electrostatic interactions between defect and defect image, so it does not treat, for example, errors due to restricted relaxation. Scaling the Freysoldt-corrected energies recovers similar results and uncertainties to scaling the uncorrected values of $E_{\text{Relaxation}}$ and E_{Transfer} , namely 0.43 ± 0.01 eV for $E_{\text{Relaxation}}$ and 1.98 ± 0.02 eV for E_{Transfer} .

Figure 8: Positions of filled and empty Ce4f states relative to the valence band edge (VBE), for experiment, for LDA+U in the 96 atom supercell for LDA+U in the lone polaron (infinite supercell) limit as obtained by finite size scaling of calculated values for 12, 96 and 324 atom supercells. Filled (polaronic) levels are shown as calculated using E_{DOS} (dotted, red), $E_{\text{Localization}}$ (solid, green), and E_{Transfer} (dashed, blue). Empty Ce4f states are shown starting from the lower limit solid (maroon) line and the shaded region above it.

In figure ??d), we show the variation of the adiabatic barrier height, $E_{\text{Adiabatic}}(L)$, with supercell size. The variation with supercell size is again modest, and scaling using equation ?? as above gives $E_{\text{Adiabatic}}^{L \rightarrow \infty} = 0.15 \pm 0.02$ eV. The residual er-

rors are about +0.05 eV and +0.03 eV in the 96 and 324 atom supercells, respectively. This 0.15 ± 0.02 eV barrier is a little small compared to most of the experimental estimates which lie around 0.19–0.22 eV, but at least that of Blumenthal and Hofmaier was as low as 0.16 eV.[?] It may also be that the true adiabatic hopping barrier for a lone polaron *should* be this low, and that the value measured by the experimentalists, despite their best efforts, still includes some averaging over larger barrier contributions such as at grain or twinning boundaries, temporary trapping at impurities or vacancies, or interactions between polarons. Another factor could be the degree of uniformity of practical polarons concentrations, since both experimental and calculated barriers increase with concentration.

7. Conclusions

We have studied the properties of Ce4f electron-polarons in CeO₂ (ceria) using DFT with a variety of functionals: LDA+*U*, GGA+*U*, and the hybrids HSE03, HSE06, PBE0 and B3LYP. Unlike pure LDA and GGA, all of these are qualitatively able to localize the Ce4f electrons as polarons, but the predicted properties do vary.

We have calculated and compared three different estimates of the gap level corresponding to polarons: the DOS level E_{DOS} , and two numbers derived from total energies: the transfer level $E_{Transfer}$, which identifies the gap level relative to the VBE, and the relaxation energy $E_{Relaxation}$, which identifies the level, $E_{Localization}$, relative to the Ce4f(Empty) band. Using LDA+*U* and GGA+*U* in a 96 atom supercell, we find mutually consistent values of these energies which are all reasonably close to experiment, although the $O2p \rightarrow Ce4f$ bandgap is slightly underestimated. The hybrids tend to slightly overestimate this gap, with the exception of PBE0 which overestimates it by 45%, and more significantly overestimate the gap levels.

We find that the spatial size of the polarons is in the Holstein “small polaron” regime, as expected. With all of these functionals, the structural distortions are largely limited to nearest neighbours. The charge localization using LDA+*U* and GGA+*U* is

also in this range (though with a tail spreading further out beyond the nearest neighbours) but it is rather less using the hybrids, where the charge was much more spread out.

Varying *U* for LDA+*U* and GGA+*U* we find that, while the degree of localisation shows a plateau around the optimal *U* value, the energies E_{DOS} , $E_{Transfer}$ and $E_{Relaxation}$ do not, instead being sensitive to the precise choice of *U*. On the other hand varying the screening range parameter μ for the HSE-type functionals from PBE through to PBE0 has a strong effect on the empty Ce4f states, but rather little effect on the gap state energy, at least once the Ce4f electron has become localized. Comparing these variations suggests that the improvements in the description of ceria polarons obtained by adding the “*U*” to LDA or GGA are largely due to changes in the description of the filled Ce4f states, while the improvements obtained by adding some HF exchange to GGA are largely due to changes in the description of the empty Ce4f states.

Regarding the polaron hopping barriers, we have demonstrated that there *is* enough correlation present in advanced DFT functionals to allow the calculation of adiabatic polaron hopping energy barriers ($E_{Adiabatic}$), and to obtain at least rough estimates of the diabatic barriers ($E_{Diabatic}$). Our LDA+*U*=6eV value for $E_{Adiabatic}$ is comparable to experiment and our overlap matrices $V_{12} = (E_{Diabatic} - E_{Adiabatic})$ estimated with the same functional are similar to those obtained by higher level methods.[?] However, the $E_{Adiabatic}$ values obtained using the hybrids in particular are badly underestimated as compared to experiment.

Finally, with LDA+*U*=6eV in 12, 96 and 324 atom supercells we have examined the finite size errors of the supercell approximation, in order to extract the energetics of lone polarons. These errors turn out to be fairly mild in this case: The energy of the polaron level in the bandgap is still estimated to lie around 1.7–2.0 eV above the VBE, with a value of the polaron relaxation energy of ≈ 0.4 eV, in reasonable agreement with experiment. We noted that Freysoldt corrections[?] alone only correct $\frac{1}{3} \rightarrow \frac{1}{2}$ of the actual error. The adiabatic barriers, meanwhile, scale to ≈ 0.15 eV, in reasonable agreement with the lowest experimental value (0.16 eV[?]) but a little low compared to

the 0.19-0.21 eV of most other experiments.???? This could be due to limitations in the DFT, or possibly to the experiments not directly measuring the true bulk lone polaron barriers themselves, and/or the effects of non-uniform polaron concentrations, since the barriers are higher at higher concentrations.

In summary: we have presented two threads of new results. 1: We have presented a detailed and consistent description of electron-polarons in ceria, obtained using DFT with LDA+*U*, GGA+*U* and four hybrid functionals, and have compared this to experiment. 2: We have presented a comparison of the three contrasting methods commonly used to estimate where in the bandgap the polaron level lies, and examined the use of standard (un-constrained) plane-wave DFT with a variety of functionals to calculate adiabatic polaron hopping barriers and estimate the diabatic barriers. All the functionals considered produce qualitatively correct descriptions of localised Holstein “small polarons” with an energy level in the upper part of the $O2p \rightarrow Ce4f$ bandgap and a barrier to polaron hopping and charge transport. However, we have shown that the hybrids all significantly underestimate the polaron hopping barrier, overestimate the gap and tend to place the polaron gap level proportionately too high within it. So, as with the description of ceria bulk properties, (and at least in the absence of, say, adhered molecules,) the best and most internally consistent description of polarons in ceria, as compared to experiment, is obtained using LDA+*U*=6eV, where we find:

- A gap level for lone polarons of ~ 1.7 -2.0 eV above the VBE, with a relaxation energy value of ~ 0.4 eV.
- A polaron size of ~ 1 lattice spacing.
- An adiabatic hopping barrier for lone polarons of $\sim 0.15 \pm 0.02$ eV.

Note added at proof stage: While publishing our paper we became aware that Sun, Huang, Wang and Janotti published a study of charge carriers in ceria using GGA+*U* and HSE06 (?). For those two functionals, they give values for EDOS, Relaxation and Eadiabatic which are much in keeping with ours, although they do find a larger value for Eadiabatic than we do when using HSE06. The difference may be at least partially explained by

differences in k-point integration. Beyond those values, however, Sun et al. focus on carrier mobilities and interactions, presenting results also for vacancies and vacancy-polaron complexes, while we focus on the properties of the polarons themselves, and details of how to model them. We use six functionals (GGA+*U* and HSE06 plus LDA+*U*, PBE0, HSE03 and B3LYP) in our work

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