Refined embedded-cluster calculations for trapped hole bipolarons in BaTiO$_3$

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Abstract. Embedded-quantum-cluster calculations are used to investigate the formation of hole-type bipolarons in BaTiO$_3$. These simulations improve on our recent results because of the exact performance of geometry optimizations of the embedded quantum cluster. Moreover, ion relaxations and electron correlations have been treated consistently. The modelling of correlations includes Møller–Plesset perturbation theory to second order (MP2) and density functional theory (DFT) beyond the local density approximation. Both defect-induced crystal relaxations and electron correlation contributions are necessary in order to stabilize trapped hole bipolarons in BaTiO$_3$.

Recent photo-ESR-based investigations [1] suggested that diamagnetic hole-type defects significantly participate in the light-induced charge-transfer processes observed in BaTiO$_3$. It has been speculated that these defects consist of O_2^{2-} peroxy ions possessing a spin-singlet ground state. In a previous publication [2] (hereafter denoted as I) we presented shell-model-based simulations of such hole-type bipolarons which are trapped at suitable acceptor-type impurity cations. Superior calculations employing an approximate embedded-quantum-cluster approach have been performed for bipolarons associated with Mg_{Ti}^{2+}. In this way the local electronic defect structure could be explicitly taken into account. The embedded-cluster calculations were based on an *ab initio* molecular orbital description employing Hartree–Fock (HF) theory and preliminary configuration interaction (CI) expansions. The quantum cluster was chosen corresponding to the formula $MgO_6Ba_8Ti_6$. Split-valence-quality basis sets augmented with polarizing d-type functions have been employed for the central MgO_6 fragment, whereas bare effective-core potentials (ECP) [3] were used to represent the Ba and Ti cations at the cluster boundary. These pseudopotentials simulate important ion-size effects of the respective cations. The embedding lattice has been treated in the framework of a shell-model pair-potential approach. Pair potentials were also chosen to mediate the short-range cluster–lattice interactions. For details of these calculations, refer to our previous publication (I). Our earlier investigations suggested that defect-induced crystal relaxations and electronic correlation contributions are necessary in order to stabilize the hole-type bipolarons against competitive defect structures, of which the linear O^-–Mg^{2+}–O^- complex under consideration, with the holes localized on two adjacent oxygen ligands, provides an important example.

In our previous work two major approximations were used, i.e., first, the determination of the equilibrated cluster geometry using a pair-potential description and, second, the neglect of full multipole consistency during the relaxation step for the embedding lattice (see [4]

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and I for technical details). The second simplification is of minor importance for present purposes, because the charges of the cluster ions calculated by a Mulliken population analysis are close to their formal counterparts. A cluster model based on formal integral charges sufficiently reproduces the multipole moments of the quantum cluster (see I). The agreement is particularly satisfactory for the linear complex and for bipolarons with bond lengths close to the calculated equilibrium value. The first approximation, on the other hand, needs a careful re-examination. It is the goal of this letter to demonstrate corresponding implications. Further improvements refer to the performance of embedded-cluster calculations employing density functional theory (DFT). In this manner the consistent combination of electron correlations and crystal relaxations has been most efficiently accomplished.

The specification of basis sets and effective-core potentials for the $MgO_6Ba_8Ti_6$ quantum cluster is the same as in I. I have found that the augmentation of additional basis functions does not provide significant changes. All subsequent embedded-cluster calculations have been performed employing the CADPAC program package [5]. Besides performing traditional quantum chemical *ab initio* calculations (Hartree–Fock, correlation interaction expansions and Møller–Plesset perturbation theory) this code also allows DFT-type simulations based on the Kohn–Sham procedure. CADPAC employs Gaussian-type basis functions and a numerical quadrature of all integrals which are related to the effective one-electron exchange–correlation potential. Two choices have been used in order to approximate the unknown exact exchange–correlation functional, i.e. the local spin-density *ansatz* of Vosko, Wilk and Nusair [6] (the VWN-LSDA), and a more advanced functional which combines the exchange functional due to Becke [7] and the correlation functional derived by Lee, Yang and Parr [8]. Subsequently, this combined exchange–correlation functional is abbreviated as the BLYP functional. It is emphasized that the BLYP functional improves on the local density approximation.

In order to perform cluster geometry optimizations which are consistent with the embedding crystal lattice (represented by a point-charge field) an additional program has been written which updates the total cluster energies and gradients, as calculated by any quantum chemical program such as CADPAC, by adding appropriate short-range pair-potential contributions due to the required interactions between cluster ions and embedding lattice ions. With these updates the program carries through the cluster geometry optimization using a variable-metric (quasi-Newton) minimization algorithm. Relaxations of the embedding shell-model lattice, on the other hand, were determined with the CASCADE computer program [9] which has also been employed in our previous investigations (I).

Based on these improvements I repeated the most important steps of our previous simulations in order to check their stability as well as possible changes. First, the singlet equilibrium state of trapped bipolarons has been re-examined within the Hartree–Fock scheme. *In excellent agreement with the earlier results the bipolaronic bond length is found to be 1.44 Å* which supports the idea of an embedded molecular species. However, the energy separation with respect to the linear complex increases from the previous value of 0.5 eV to 1.9 eV. The explanation for this deviation is supposed to be as follows: our earlier cluster relaxations have been essentially obtained using a pair-potential approximation. For both defect complexes only the Mg^{2+} and the O^- ions were subject to further adjustments according to the correct quantum forces. The corresponding energy gain is probably larger *in the case of the bipolaron due to the peroxy bonding effects. The linear configuration,* on the other hand, benefits more by the adjustment of the remaining cluster ions which is included only in the present investigations. In spite of the numerical deviation discussed above the general trend of defect-induced crystal distortions is to favour the formation of bipolarons. This may readily be seen by comparing different stages of a relaxation:

within a perfect lattice the energy difference between the bipolaron (with the O^- ions on neighbouring perfect-lattice positions) and the linear complex is ~6 eV. It becomes reduced to about 3.5 eV upon relaxing the O^- ions with all other cluster and embedding lattice ions remaining fixed on their perfect-lattice positions. Finally, the inclusion of complete lattice relaxation yields 1.9 eV. Two further observations are noticeable. The first concerns the localization of hole states upon crystal relaxations. As has been previously stated the bipolaronic hole states become increasingly delocalized upon separating the corresponding oxygen partners within an otherwise perfect crystal. On the other hand, the hole states remain significantly more localized if complete crystal relaxations are taken into account. Second, defect-induced crystal relaxations favour the spin-singlet state of bipolarons over the spin-triplet state. In agreement with our previous investigations there is an equilibrium separation at 1.96 Å related to the triplet state. Energetically, this configuration is 1.71 eV less favourable than the singlet equilibrium state.

All HF-based simulations consistently show that peroxy bipolarons are unstable within Hartree–Fock theory. I emphasize that this particular result is not unexpected, because HF theory is known to underestimate the molecular bonding properties. It is instructive to compare the present bipolaron simulations with calculations for some relevant free molecules, i.e. for the isoelectronic F_2 and O_2^{2-} molecules. The predicted instability of isolated F_2 within HF theory (see also [10], for example) parallels our findings for bipolarons. The HF binding energy of the fluorine molecule is +1.48 eV.
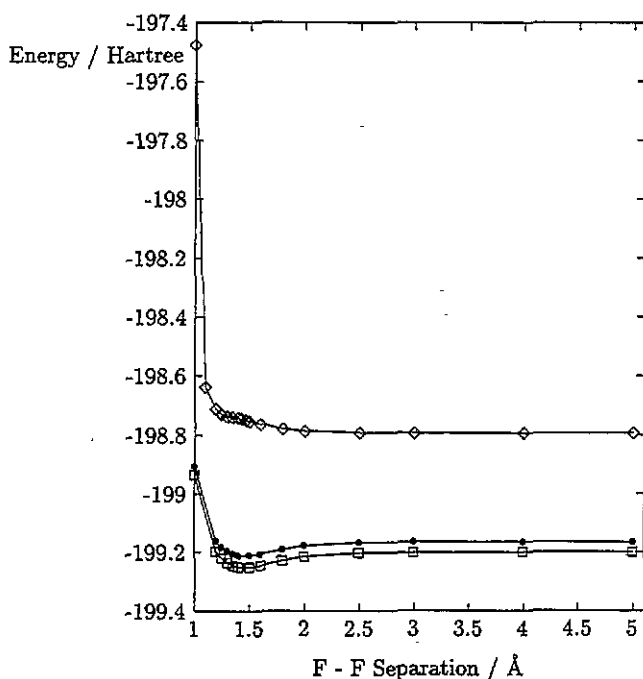

Figure 1. Potential energy curves (spin-singlet ground state) for isolated F_2 molecules: symmetry-broken Hartree–Fock ($\lozenge$), MRSDCI ($\bullet$) and MRSDCI + Q ($\square$) results.

HF potential energy curves (PEC) for F_2 molecules and (isolated) O_2^{2-} ions are shown in figures 1 and 2, respectively. Due to the unscreened Coulomb repulsion between the oxygen ions the energy decreases with increasing bond length. I recall in this context that it
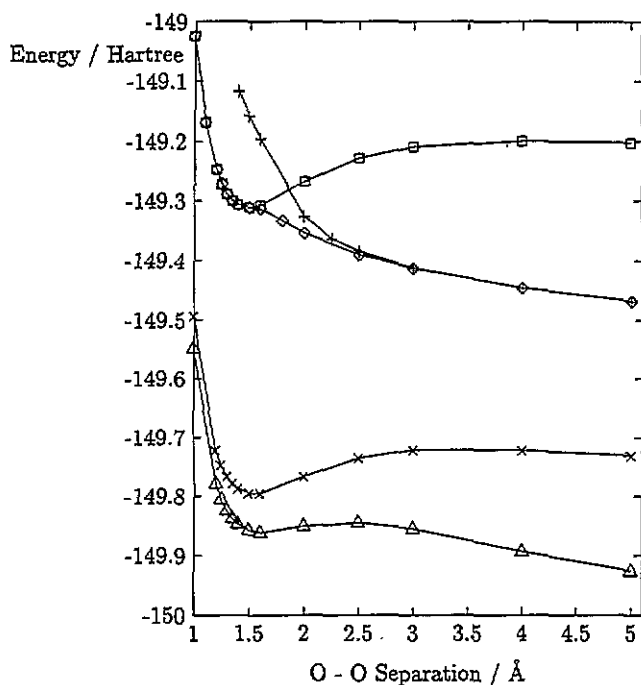
Figure 2. Potential energy curves for isolated O_2^{2-} molecular anions: symmetry-broken spin-singlet and spin-triplet curves obtained using the Hartree–Fock approach ($\Diamond$ and $+$, respectively), the singlet-state Hartree–Fock curve based on a symmetry-restricted one-determinant wavefunction ($\Box$), and the singlet state including correlations: the MRSDCI ($\times$) and the MRSDCI + Q method ($\triangle$).

can be dangerous to imply restrictions due to the molecular symmetry in the determination of one-electron orbitals which are used to construct the all-electron HF wavefunction. Such symmetry-conserving calculations may well provide the wrong dissociation states, which is a manifestation of the so-called 'symmetry dilemma' of HF theory [11, 12]. Corresponding effects are exemplified by the '$\Box$'-marked curve in figure 2. Artificially, this curve yields a binding energy of -2.9 eV for O_2^{2-}. Moreover, there is no Coulomb repulsion between the two O^- anions using this symmetry-restricted solution. The non-restricted '$\Diamond$'-curve in figure 2 yields the correct dissociation behaviour; as expected this spin-singlet state agrees with the spin-triplet state $(+)$ at large separations. The HF-based dissociation energies of various molecular oxygen anions quoted in [13] are related to corresponding symmetry-restricted calculations involving the wrong dissociation state which is built up of symmetry-restricted delocalized one-electron orbitals. For example, the dissociation energy of O_2^- is not 10.6 eV based on restricted HF theory but 1.0 eV as derived from the symmetry-broken one-determinant solution to the ground state. Similarly, my symmetry-restricted HF calculations for F_2 simulate a dissociation energy of $+8.9$ eV instead of the correct -1.48 eV! In fact, the exact molecular wavefunctions must possess the symmetry of the molecule considered. Therefore, wavefunction-based *ab initio* descriptions should provide schemes for obtaining symmetrized wavefunctions. In the present situation this could be accomplished by the proper superposition of symmetry-broken one-determinant wavefunctions. This method goes beyond HF theory and represents a simple example of the non-orthogonal configuration interaction approach [14]. However, within HF theory

the symmetry-broken solutions are sufficient for obtaining reliable estimates of molecular potential energy curves.

The similarity of F_2 and *embedded* O_2^{2-} molecules suggests that the relaxed lattice effectively screens the O^- charges. Anticipating this similarity between F_2 and *embedded* O_2^{2-} it appears not very surprising that HF theory is unable to predict a stable bipolaron state. It is therefore mandatory to include electron correlations. I consider first the isolated molecular species. PECs for isolated F_2 and O_2^{2-}, which were obtained from multi-reference configuration interaction calculations employing single and double electronic excitations (MRSDCI + Q), are also displayed in figures 1 and 2. The '+Q' denotes corrections made to the 'bare' MRSDCI results in order to guarantee size consistency. This is achieved on the basis of the Davidson formula [15]. Whereas for F_2 the '+Q'-correction is of minor importance, it becomes necessary in the calculations for O_2^{2-}. Generally, the neglect of size-consistency corrections leads to an underestimation of correlations at larger separations and, correspondingly, to an overestimation of binding energies (compare the '×'- and the 'Δ'-curves in figure 2, for instance).

In the case of the fluorine molecule the calculated bond length corresponds to 1.45 Å and the binding energy is −1.4 eV (the corresponding experimental values are 1.41 Å and −1.7 eV). In comparison density functional theory (DFT) produces the following numbers:

(i) from the VWN-LSDA: $r_B = 1.39$ Å, $E_B = -3.4$ eV;
(ii) from the BLYP functional: $r_B = 1.43$ Å, $E_B = -2.2$ eV.

These results show that the LSDA particularly overestimates molecular binding energies. The results are significantly improved by applying the BLYP exchange–correlation functional.

For isolated peroxy anions the CI calculations predict a local minimum corresponding to a metastable state close to 1.5 Å. At larger oxygen–oxygen separations the Coulomb repulsion overcomes the bonding effects. The MRSDCI + Q curve is parallel to the correct HF curve in this regime.

It is now instructive to discuss the corresponding results for the embedded O_2^{2-} peroxy molecules. As was previously suggested (see I) the binding energy of bipolarons can be estimated by the energy difference $\Delta := E(\text{BP}) - E(O^--Mg-O^-)$, since, based on shell-model results, the linear O^--Mg-O^- complex is only slightly bound in $BaTiO_3$. The qualitative trends which have already been found for the isolated molecular species remain true in the case of the bipolarons:

(i) from MP2: $\Delta = -0.41$ eV;
(ii) from the VWN-LSDA: $r_B = 1.48$ Å, $\Delta = -2.1$ eV;
(iii) from the BLYP functional: $r_B = 1.55$ Å, $\Delta = -1.13$ eV.

Considering the MgO_6 complex I had recourse to direct MP2 calculations instead of performing MRSDCI-type calculations which need a huge amount of computer storage capacity. In the 'direct' mode all two-electron integrals are recalculated each time they are required. This procedure reduces the necessary disk storage capacity. Further, Møller–Plesset perturbation theory is known to be size consistent in each order [16]. With the exception of the MP2 results which were based on the relaxed HF cluster geometry all calculations employ their consistently relaxed crystal lattice. The above results provide an ordering of the correlation treatments similar to that found for the isolated molecules. The quantum chemical descriptions of correlations (in MP2) approach the exact binding energy from below, whereas the BLYP functional and particularly the LSDA are expected to overestimate the bonding correlations. The correct binding energy is supposed to be closer to

the BLYP functional result than to that from MP2, because MP2 (as well as the earlier single-reference SDCI + Q results, see I) may well underestimate electron correlations within the MgO_6 complex. The MP2 and SDCI + Q methods both predict a correlation energy gain of about 2 eV in favour of hole-type bipolarons.

In conclusion the present investigations demonstrate that defect-induced crystal relaxation and electronic correlations are necessary to stabilize trapped hole-type bipolarons in $BaTiO_3$. Crystal relaxations increase the localization of bipolaronic hole states and lead to a spin-singlet ground state. In short, relaxations of the host lattice support the idea of an embedded O_2^{2-} molecule with electronic properties being similar to the isolated F_2 dimer. In particular, HF theory predicts both species to be unstable. In both cases the ultimate stability is determined by the electronic correlation contributions to molecular bonding.

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