A periodic equation-of-motion coupled-cluster implementation applied to $F$-centers in alkaline earth oxides

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We present an implementation of equation of motion coupled-cluster singles and doubles (EOM-CCSD) theory using periodic boundary conditions and a plane wave basis set. Our implementation of EOM-CCSD theory is applied to study $F$-centers in alkaline earth oxides employing a periodic supercell approach. The convergence of calculated electronic excitation energies for neutral color centers in MgO, CaO and SrO crystals with respect to orbital basis set and system size is explored. We discuss extrapolation techniques that approximate excitation energies in the complete basis set limit and reduce finite size errors. Our findings demonstrate that EOM-CCSD theory can predict optical absorption energies of $F$-centers in good agreement with experiment. Furthermore, we discuss calculated emission energies corresponding to the decay from triplet to singlet states, responsible for the photoluminescence properties. Our findings are compared to experimental and theoretical results available in literature.

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I. INTRODUCTION

Density Functional Theory (DFT)\cite{1, 2} using approximate exchange and correlation energy density functionals is arguably the most successful ab initio approach to compute materials properties. Its application goes beyond ground state properties by providing a reference or starting point for methods that treat excited-state phenomena explicitly. In this context, theories such as Time-Dependent Density Functional Theory (TD-DFT)\cite{3, 4} and the GW approximation\cite{5} are widely-used to tackle excited states in molecules and solids\cite{6, 7}. Nonetheless, they often suffer from a strong dependence on the DFT reference calculation. In the case of TD-DFT, albeit being an exact theory, results depend strongly on the choice of the approximate exchange and correlation density functional. Similarly, so-called non-selfconsistent $G_0W_0$ quasiparticle energies depend strongly on the Kohn-Sham orbital energies, whereas fully self-consistent GW calculations are not as often performed and do not necessarily improve upon the accuracy compared to $G_0W_0$\cite{8}. To compute charge neutrality preserving optical absorption energies from the electron addition and removal energies obtained in the GW framework, it is necessary to account for the exciton binding energy. Excitonic effects are often approximated using the Bethe-Salpeter equation (BSE)\cite{9}. We note that despite the high level of accuracy and efficiency of GW-BSE calculations\cite{10}, many choices and approximations have to be made in practice that are difficult to justify in a pure ab initio framework. Therefore, it seems worthwhile to explore alternative methods that are less dependent on DFT approaches.

Coupled-Cluster (CC)\cite{11–13} formulations are widely-used in the field of molecular quantum chemistry for both the ground state and excited states via the Equation of motion Coupled-Cluster (EOM-CC) formalism\cite{14}. Ground state CC theories such as Coupled Cluster Singles Doubles (CCSD) and perturbative triples (CCSD(T))\cite{15, 16} have become one of the most successful methods in molecules in terms of their systematically improvable accuracy and computational efficiency. Likewise, EOM-CC methods are routinely applied to molecular systems with great success\cite{17–21}. However, we stress that the computational cost of CC theories is significantly larger than that of Green’s function based methods mentioned above. Nonetheless, several studies have focused on making use of these wavefunction methods also in solids to study ground and excited state properties\cite{22–24}. While Equation Of Motion (EOM) type methods are well understood and benchmarked in finite systems, this is less so for periodic systems, where ongoing efforts are made towards applications in solids. Previous applications of EOM type methods have focused on electronic band structures using the Ionization Potential EOM-CC (IP-EOM-CC) and Electron Attachment EOM-CC (EA-EOM-CC) extensions\cite{23, 23–26} as well as its Electron excitation EOM-CC (EE-EOM-CC) extensions\cite{27, 28}, all of which are based on Gaussian basis sets. For local phenomena, such as defect excitation energies, several studies have been performed employing cluster models of the periodic structures\cite{29, 30}. One of the main challenges in these calculations is to achieve a good control over the finite basis set and system size errors, which is often achieved using extrapolation techniques. In this manuscript, we study excited state properties of point defects in solids, computed on the level of EE-EOM-CC. Understanding impurities in solids is important for both theoretical and practical reasons. Lattice defects affect bulk properties of the host crystal and both the understanding of ground and excited-state properties is essential for these systems\cite{31, 32}. Here, we focus on color centers in the alkaline earth oxide crystals MgO, CaO and SrO in the rock salt structure. Remov-
ing an oxygen atom from these systems results in so-called \(F\)-centers that can be filled by 2 \((F^0)\), 1 \((F^+)\) or 0 \((F^{2+})\) electrons. The corresponding one-electron states are stabilized by the Madelung potential of the crystal and their electron density is in general localized in the cavity formed by the oxygen vacancy. These defects are typically produced by neutron irradiation [33] or additive colorization [34]. Much effort has been made to elucidate the exact mechanism of the luminescence of \(F\)-centers in MgO, CaO and SrO [35, 36]. The ground and excited state properties of these vacancies are of importance for a wide range of technological applications including color center lasers. Furthermore, vacancies of oxides are of general importance for understanding their surface chemistry and related properties. In this work we will concentrate on the diamagnetic \(F^0\)-center. The trapped electrons can be viewed as a pseudo-atom embedded in a solid, where the optical absorption and emission between ground and low-lying excited states is characterized by the electron transfer between 1s into 2s or 2p one-electron states. Initial theoretical studies of these defects were already performed in the 1960s and 1970s using effective Hamiltonians [37–39]. Modern ab initio studies of the \(F\)-center in MgO have employed cluster approaches in combination with quantum chemical wavefunction based methods [30], fully periodic supercell approaches in combination with the \(GW\)-BSE approach [40, 41] or Quantum Monte Carlo calculations [42]. In this work we seek to employ a periodic supercell approach and a novel implementation of Equation of motion CCSD (EE-EOM-CCSD) theory using a plane wave basis set. In addition to the \(F^0\)-center in MgO, we will also study \(F\)-centers in CaO and SrO. We note that EE-EOM-CCSD theory is exact for ground and excited states of two electron systems and is therefore expected to yield very accurate results for the \(F^0\) center in alkaline earth oxides. We will discuss different techniques to correct for finite basis set and supercell size errors and demonstrate that EE-EOM-CCSD theory can be used to compute accurate absorption and emission energies compared to experiment without the need for adjustable parameters and the ambiguity caused by the choice of the starting point.

The following is a summary of the structure of this work. In Section II we give a brief overview of the employed theoretical and computational methods used to compute excitation energies including extrapolation techniques that are needed to approximate to the complete basis set and infinite system size limit. Section III presents the obtained results of the defect calculations and draws a comparison between this work and available experimental and theoretical results from the literature.

II. THEORY AND METHODS

We start this section by giving a brief description of the employed CC methods followed by a discussion of the computational details.

A. CCSD theory

The CC approximation is based on an exponential \textit{ansatz} for the electronic wavefunction [13, 43] acting on a single Slater determinant \(|0\rangle\),

\[
|\Psi\rangle_{\text{CC}} = e^{\hat{T}} |0\rangle
\]

where the \textit{cluster operator} consists of second-quantized neutral excitation operators

\[
\hat{T} = \sum_{\mu} t_{\mu} \hat{r}_{\mu}, \quad t_{\mu} \in \mathbb{C}
\]

with \(\mu\) labeling excitation configurations. For instance, when considering only singles and doubles excitations (CCSD) the unrestricted CCSD cluster operator is given by

\[
\hat{T} = \sum_{a,i} t_{a,i} a_{a\dagger}^i + \sum_{a,b,i,j} t_{a,b,i,j}^a a_{a\dagger}^i a_{b\dagger}^j a_j^i
\]

where the set of indices \(\{a, b, c, \ldots\}\) denote virtual or unoccupied spin orbitals and \(\{i, j, k, \ldots\}\) denote occupied spin orbitals. Orbitals are occupied or unoccupied with respect to the reference Slater determinant \(|0\rangle\), which may come for instance from a Hartree-Fock (HF) or a DFT calculation. Here, we will restrict the discussion to the case of CCSD. Applying the CC \textit{ansatz} to the stationary many-body electronic Schrödinger equation results in

\[
\hat{H} |0\rangle = e^{-\hat{T}} \hat{H} e^{\hat{T}} |0\rangle = E_{\text{CC}} |0\rangle \tag{1}
\]

where \(E_{\text{CC}}\) is the coupled cluster energy, and we have implicitly defined the similarity transformed Hamiltonian \(\hat{H}\). The state \(|\Psi_{\text{CC}}\rangle\) is parametrized by the coefficients \(t_{\mu}\), which can be obtained by projection. In the case of CCSD one projects the Schrödinger equation onto the singles and doubles sections of the Fock space

\[
E_{\text{CC}} = \langle 0 | \hat{H} | 0 \rangle \tag{2}
\]

\[
0 = \langle 0 | \hat{a}_{a\dagger}^i \hat{a}_a \hat{H} | 0 \rangle \tag{3}
\]

\[
0 = \langle 0 | \hat{a}_{a\dagger}^i \hat{a}_{j\dagger}^j \hat{a}_b \hat{a}_a \hat{H} | 0 \rangle. \tag{4}
\]

Equations (2–4) are a set of coupled non-linear equations in terms of the amplitudes \(t_{ai}\) and \(t_{ij}\) that are solved by iterative methods.

B. EE-EOM-CCSD theory

A common way to obtain excited states based on the CC theory is through diagonalizing the similarity transformed Hamiltonian \(\hat{H}\) in a suitable subspace of the Fock space [14]. We are going to present the neutral variant of this approach, also called electronically excited equation of motion, for which the number of electrons is conserved.
FIG. 1: Geometry of neutral F-center in MgO. Red and orange spheres correspond to oxygen and magnesium atoms, respectively. The yellow isosurface was computed from the localized electronic states in the band gap of MgO that originates from the two trapped electrons. δ measures the displacement along the $A_{1g}$ vibrational mode with the Mg atoms out of their equilibrium position in the bulk structure and was deliberately chosen larger for this figure to emphasize the effect of lattice relaxation.

In consequence, restricting from now on again the analysis to singles and doubles excitations, the ansatz for an excited state $\hat{R}|\Psi_{CC}\rangle$ is

$$\hat{H}\hat{R}|\Psi_{CC}\rangle = \hat{H}\hat{R}e^{\hat{T}}|0\rangle = E_R\hat{R}|\Psi_{CC}\rangle$$

where

$$\hat{R} = r_0 + \sum_{a,i} r_{a}^{a}\hat{a}_{i}^{\dagger}\hat{a}_{i} + \sum_{a,b,i,j} r_{a,b}^{i,j}\hat{a}_{i}^{\dagger}\hat{a}_{j}^{\dagger}\hat{a}_{j}\hat{a}_{i}, \quad r_{\mu} \in \mathbb{C}$$

is a linear excitation operator and $E_R$ is its excitation energy. Equation (5) is equivalent to a commutator equation only involving $\hat{H}$ and the excitation energy difference $\Delta E_R$ between $E_R$ and the correlated ground state $E_{CC}$.

$$[\hat{H}, \hat{R}]|0\rangle = (\hat{H}\hat{R})_c |0\rangle = (E_R - E_{CC})\hat{R}|0\rangle = \Delta E_R\hat{R}|0\rangle.$$  

Equation (7) motivates the name equation of motion due to its resemblance to the time-dependent Heisenberg picture differential equation for the time evolution of an operator.

C. Computational methods and details

Here, all EE-EOM-CCSD calculations of defective supercells employ a HF reference. The HF calculations are performed using the Vienna ab initio simulation package (VASP) [44] and a plane wave basis set in the framework of the projector augmented wave (PAW) [45] method. The energy cutoff for the plane wave basis set is 900 eV. The defect geometries have been relaxed on the level of DFT-PBE, starting from a defective geometry with the corresponding equilibrium lattice constant (MgO: 4.257 Å, CaO: 4.831 Å, SrO: 5.195 Å) keeping the lattice vectors and volume fixed. In this work we study defective 2×2×2, 3×3×3 and 4×4×4 fcc supercells containing 15, 53, and 127 atoms, respectively. The oxygen vacancy results in an outward relaxation of the alkaline earth atoms away from the cavity created by the oxygen vacancy. This outward relaxation strongly overlaps with the vibrational mode $A_{1g}$ and is illustrated in Fig. 1. While the DFT-PBE calculations have been carefully checked for convergence with respect to the k-point mesh used to sample the first Brillouin zone, all HF and post-HF calculations employ the Γ-point approximation.

We have implemented Unrestricted CCSD (UCCSD) and EE-EOM-CCSD in the Coupled Cluster For Solids (cc4s) code that was previously employed for the study of various ground state properties of periodic systems [22, 46]. The employed Coulomb integrals and related quantities were calculated in a completely analogue manner. Our UCCSD implementation is based on the intermediate amplitudes approach of Stanton et al. [47]. On the other hand, our EE-EOM-CCSD implementation uses intermediates for the similarity transformed Hamiltonian $e^{-\hat{T}}\hat{H}e^{\hat{T}}$ from Stanton et al. [14] and Shavitt et al. [48]. We use the Cyclops Tensor Framework (CTF) [49] for the implemented computer code, which enables an automated parallelization of the underlying tensor contractions.

The diagonalization of the similarity transformed Hamiltonian is done using a generalized Davidson solver [50, 51] which enables the calculation of EE-EOM-CCSD energies without explicit calculation of the left eigenvectors. For the initial guess of the eigenvectors, we use the one-body HF excitation energies and corresponding Slater determinants. The UCCSD and EE-EOM-CCSD calculations have been performed using only a small number of active HF orbitals around the Fermi energy of the employed supercells. Most occupied orbitals at low energies are frozen and the same applies to all unoccupied orbitals above a certain cutoff energy. The following sections summarize the benchmarks of the implemented EE-EOM-CCSD code and investigate the convergence behavior of the computed excitation energies with respect to the number of active orbitals as well as system size.

1. Benchmark results

In the following we discuss benchmark results of our EE-EOM-CCSD implementation and outline our approach to identify the spin multiplicity attributed to the excited states. To verify the implemented expressions, we have compared the computed EE-EOM-CCSD excitation energies to results computed using a well-established quantum chemical code NWCHEM [52]. As most quantum chemical codes (including NWCHEM) employ atom-centered Gaussian basis sets, it was also necessary to implement an interface that reads the orbital coefficients from NWCHEM and employs the LIBINT2 [53] library to compute corre-
sponding integrals. As test systems we have selected the neon atom and the water molecule in the \textit{aug-cc-pvdz} basis. All computed UCCSD energies using HF and DFT reference determinants achieve an excellent agreement (8 significant digits) between both codes. For EE-EOM-CCSD calculations, the singlet states computed by \textsc{Nwchem} were also obtained using our EE-EOM-CCSD implementation with similar convergence behavior and in excellent agreement (8 significant digits). We can identify the triplet and the singlet state in our output by using spin-flip EE-EOM-CCSD \cite{54} and comparing the degeneracy of the states computed with and without spin-flip excitations. In future work we will implement the direct computation of the spin expectation value.

2. \textit{Orbital basis convergence of excited states}

All presented findings in this section have been obtained for the $F$-center in MgO. However, the corresponding findings for CaO and SrO are qualitatively identical unless stated explicitly.

We first seek to investigate the character of the employed HF orbitals and the convergence of the computed excitation energies with respect to the canonical orbital basis set size. The HF orbitals have been computed for a defective $2 \times 2 \times 2$ MgO supercell containing 15 atoms. Figure 2 depicts the energy levels around the Fermi energy and isosurfaces of charge densities computed for the defect states. The occupied state with the highest one-electron energy corresponds to the occupied defect state and its orbital energy is located in the gap of the bulk crystal. Its charge density is well localized in the cavity created by the oxygen vacancy. In the thermodynamic limit (big supercells or dense $k$-meshes), the direct and fundamental gap of pristine MgO is 15.5 eV on the level of HF theory \cite{55}, which is significantly larger than the experimental gap of about 7.8 eV. The neglect of corelation effects in HF theory overestimates band gaps for a wide range of simple semiconductors and insulators. The orbital ordering between defect and bulk states depicted in Fig. 2 is qualitatively identical to the one observed for CaO and SrO. However, we stress that in contrast to MgO, CaO and SrO exhibit an indirect band gap with a conduction band minimum at the Brillouin zone boundary.

We note that the supercells investigated in this work contain up to 127 atoms, corresponding to more than 1000 valence electrons. The computational cost of EE-EOM-CCSD theory scales as $\mathcal{O}(N^6)$, where $N$ is some measure of the system size. In particular, the cost for some of the most important tensor algebraic operations scales as $\mathcal{O}(N_o^4 N_v^2)$ and $\mathcal{O}(N_o^2 N_v^4)$, where $N_o$ and $N_v$ refer to the number of occupied and virtual orbitals, respectively. Additionally, the memory footprint of our implementation scales as $\mathcal{O}(N^4)$. Due to the steep scaling of the computational cost, an explicit treatment of all electrons on the level of EE-EOM-CCSD becomes intractable and renders it necessary to freeze a large fraction of the occupied and virtual HF states. In the following we will investigate the convergence of the computed excitation energies with respect to the number of active virtual and occupied states.

We first investigate the convergence of EE-EOM-CCSD excitation energies with respect to the virtual orbital basis set. Among the 61 occupied spatial HF orbitals we keep only the four orbitals active with the highest energy. Furthermore, we only investigate many-electron excited states with $r_1^a$ excitation amplitudes that
correspond to a significant charge transfer from the occupied s-like defect state to the virtual p-like defect states as illustrated in Fig. 2. Fig. 3 depicts the convergence of the EE-EOM-CCSD excitation energies that we assign to local excitations of the $F$-center. In passing we note that EE-EOM-CCSD theory predicts a number of excited states that describe electronic excitations with charge transfer from the defect to bulk states, which will not be explored in this work. The electronic ground state of the neutral $F$-centers studied in this work is a singlet state. The lower and higher excitation energies shown in Fig. 3 correspond to a singlet-triplet and singlet-singlet transition energy, respectively. We observe for both excitation energies a $1/(N_v + N_o)$ convergence to the complete basis set limit. This behavior is not unexpected and agrees with the convergence of ground state energies. Furthermore, we note that a similar convergence was observed for EE-EOM-CCSD exciton energies of bulk materials [28]. We note that it might seem advantageous to replace HF virtual orbitals with a different type of orbitals; for example, natural orbitals, to accelerate the convergence. However, we have found that these orbitals will mostly accelerate the convergence of the ground state energy, introducing large basis set incompleteness errors in the convergence of excitation energies. In this work we will employ a $1/(N_v + N_o)$ extrapolation to approximate excitation energies in the complete basis set limit of all systems.

Fig. 4 shows the employed basis set extrapolation for identical transitions in a larger $4 \times 4 \times 4$ supercell. We note that the slope of the excitation energy extrapolation is significantly steeper compared to the $2 \times 2 \times 2$ supercell shown in Fig. 3. This can be attributed to the smaller number of virtual orbitals relative to the complete basis set size for the given plane wave cutoff energy. Therefore we ignore the first 4 points in the extrapolation for all systems in the $4 \times 4 \times 4$ supercell. In the case of CaO and SrO, the basis set convergence of the excitation energies is qualitatively identical, and we employ the same orbital basis set sizes in all extrapolations.

We now investigate the convergence of the EE-EOM-CCSD excitation energies with respect to the number of active occupied orbitals, keeping a virtual orbital basis set consisting of 10 unoccupied orbitals and employing a $2 \times 2 \times 2$ supercell only. Figure 5 depicts the convergence of the lowest defect excitation energy (singlet-triplet transition) with respect to the size of the active occupied orbital space. The horizontal axis at the bottom shows the number of active occupied orbitals. The horizontal axis at the top of Fig. 5 shows the corresponding lowest HF orbital energy. Our findings demonstrate that the excitation energy increases with respect to the number of active occupied orbitals and is well converged to within a few meV using more than about 25 occupied orbitals. However, a comparison between the converged result and a minimal active occupied orbital space, consisting of the occupied defect orbital only, reveals that such a truncation introduces excitation energy errors of about 120 meV. We note that one-electron states with relative energies below $-50$ eV exhibit Mg $2p$ and $2s$ character and are therefore expected to be negligible for the computed excitation energies. From the above findings we conclude that the excitations studied in the present work exhibit a significantly larger error from the virtual orbital basis truncation than from the occupied orbital basis truncation. Due to the computational cost of EE-EOM-CCSD calculations we will therefore extrapolate
### TABLE I: Convergence of the F-center’s excitation energies in MgO, CaO and SrO for increasing supercell size. TDL corresponds to the extrapolated thermodynamic limit estimate of the respective excitation energies assuming a 1/N convergence and employing the energies of the 2×2×2 and 4×4×4 supercells. Here N is the total number of electrons in each supercell. In this case, the number of electrons is used. All energies in eV units.

| System | Supercell | 3T | 1A |
|--------|-----------|----|----|
| MgO    | 2×2×2     | 7.009 8.522 | | |
|        | 3×3×3     | 4.866 6.571 | | |
|        | 4×4×4     | 4.038 5.646 | | |
|        | TDL       | 3.660 5.281 | | |
| CaO    | 2×2×2     | 3.224 3.338 | | |
|        | 3×3×3     | 2.951 4.025 | | |
|        | 4×4×4     | 2.081 3.157 | | |
|        | TDL       | 1.936 3.134 | | |
| SrO    | 2×2×2     | 3.242 2.413 | | |
|        | 3×3×3     | 2.404 3.155 | | |
|        | 4×4×4     | 1.332 2.351 | | |
|        | TDL       | 1.206 2.343 | | |

Here, we seek to remove the remaining finite size errors of the excitation energies by performing an extrapolation to the infinite system size limit assuming a 1/N convergence, where N is the total number of electrons in each supercell. This approach is in agreement with procedures that are applied to ground state energy calculations [22, 56]. For the sake of consistency we employ only 2×2×2 and 4×4×4 supercells for the extrapolation for all three studied systems.

Our findings show that the excitation energies decrease significantly with increasing supercell size in the case of MgO. Changing the supercell size from a 2×2×2 to a 4×4×4 cell results in a lowering of the excitation energies by almost 3 eV. This relatively slow convergence is expected to originate from strongly delocalized excited defect states of the neutral F-center in MgO. We note in passing that the excitation energies of the F-centers in CaO and SrO exhibit a significantly faster convergence with respect to system size. We attribute this behavior to a more localized character of the excited F-center in CaO and SrO compared to MgO that might be explained by the significantly smaller size of the cavity formed by the oxygen vacancy in MgO compared to CaO or SrO.

### III. RESULTS

In this section we describe the photochemical process of absorption and emission in the F-center of alkaline earth oxides. We first discuss the energies of the electronically excited defect states as a function of the atomic displacements along the $A_{1g}$ vibrational mode in MgO to introduce the emission model. Next, we present our results for the absorption and emission of the F-center in MgO, where problems in the interpretation of the experimentally observed luminescence band are discussed additionally. We end this section with a discussion of the results for CaO and SrO.

#### A. Absorption and emission process in F-centers

Our analysis of the emission process is based on a Franck-Condon [57, 58] description of the defect. This is a common approach to treat emission processes in solids and molecules [39, 59, 60]. Figure 6 shows the configuration coordinate diagram along an approximate $A_{1g}$ vibrational mode for the most important EE-EOM-CCSD excited states and the UCCSD ground state singlet $^1A_{CC}$. We approximate the atomic displacement along the $A_{1g}$ mode by increasing the outward displacement of the alkaline earth atoms as depicted in Fig. 1, and keeping all other atomic positions of the employed 4×4×4 supercell fixed. The configuration curve has been computed only for MgO but serves as a qualitatively identical model for CaO and SrO. Within this picture, the absorption is given by the optically allowed transition of $^1A_{CC} \rightarrow ^1A$ at the ground state geometry in Fig. 6. Tak-
The calculation was done for a 4×4×4 cell containing 127 atoms, 4 active electrons and 64 virtual orbitals.

![Fig 6](image_url)

**TABLE II:** Obtained results from this work for the absorption and emission energies of the F-centers in MgO, CaO and SrO. The EE-EOM-CCSD results are extrapolated to the complete basis set and infinite supercell size limit in order to allow for a direct comparison between theory and experiment. The GW gaps do not correspond to optical excitation energies but are included for comparison. All energies are in eV units.

| System  | Method                  | Absorption | Emission  |
|---------|-------------------------|------------|-----------|
| MgO     | EE-EOM-CCSD             | 5.28       | 3.66      |
|         | Exp. [61]               | 5.0        | 2.4       |
|         | QMC. [42]               | 5.0(1)     | 3.8(1)    |
|         | CASPT2 [30]             | 5.44       | 4.09      |
|         | $G_0W_0@$LDA0-BSE. [40] | 4.95       | 3.4       |
|         | $G_0W_0@$LDA0 [40]      | 5.4        |           |
|         | $G_0W_0@$PBE [41]       | 4.48       |           |
|         | $GW_0@$PBE [41]         | 4.71       |           |
|         | $GW@$PBE [41]           | 5.20       |           |
| CaO     | EE-EOM-CCSD             | 3.13       | 1.93      |
|         | Exp. [62, 63]           | 3.02       | 1.93      |
|         | Exp. [61]               | 3.1        | 2.05 − 2.01 |
|         | TD-DFT@B3LYP [64]       | 3.52       | 2.1       |
|         | $G_0W_0@$PBE [41]       | 3.20       |           |
|         | $GW_0@$PBE [41]         | 3.53       |           |
|         | $GW@$PBE [41]           | 3.87       |           |
| SrO     | EE-EOM-CCSD             | 2.34       | 1.2       |
|         | Exp. [61]               | 2.4        |           |

3.15 eV [71] while for the $F^0$ center a luminescence of 2.4 eV was predicted from temperature dependent measurements of the absorption spectrum in conjunction with a simplified Huang-Rhys model approach [70].

Using EE-EOM-CCSD in combination with the outlined extrapolation techniques yields an absorption and emission energy of 5.2 eV and 3.66 eV, respectively. Previous many-body ab initio calculations using GW-BSE [40], quantum Monte Carlo [42] methods and CASPT2 [30] agree with our results for both absorption and emission to within about 0.4 eV as summarized in Table II. The calculated absorption energies are in good agreement with experimental measurements of 5.0 eV. We note, however, that the GW results (excluding the exciton binding energy) obtained for different levels of self-consistency and DFT references exhibit a significant variance ranging from 4.48 eV to 5.4 eV. Consequently, GW-BSE absorption energies are strongly dependent on the DFT reference. Furthermore, we stress that a direct comparison of the computed emission energies between the quantum chemical approaches (EE-EOM-CCSD and CASPT2) and QMC or GW is complicated by the fact that the latter approaches do not consider the emission process of the de-excitation from the excited triplet states. Instead, the emission energies computed using QMC and GW-BSE correspond to the decay from the excited singlet state in its relaxed geometry along the $A_{1g}$ mode. Nonetheless, from the results shown in Fig. 6, we conclude that these different emission energies are expected to agree to within the errors made by other ap-
proximations.

The measured experimental emission at 2.4 eV [34] and its interpretation is the topic of an ongoing debate. Initially, this peak has been attributed to the F-center and common interpretations have ranged from a singlet-triplet transition to a \( ^3T_{1u} \rightarrow ^1A_{1g} \) transition [38, 61]. However, it was first suggested by Edel et al. [34, 72, 73] that this band results from a recombination process similar to recombination processes in semiconductors. Edel and coworkers argue that the three-electron vacancy \( F^- \) recombines with the \( F^+ \)-center. Rinke et al. [40] have suggested that the 2.4 eV emission is produced when electrons in the defect orbitals recombine with the valence holes that can be produced by intense UV light irradiation. The creation of these holes is possibly also related to the concentration of \( \text{H}^+ \) impurities that are commonly present in MgO samples, especially when these have been thermochemically reduced [33, 74–77]. The presence of \( \text{H}^+ \) impurities in MgO could account for the long-lived luminescence through a hopping mechanism of the electrons from \( \text{H}^- \) to \( \text{H}^- \) impurities until they encounter an \( F^- \)-center. However, it is not immediately clear from the ab initio calculations thus far if these states are orbital and spin triplets or otherwise as has been proposed in experimental evidence and symmetry arguments [61]. It has been noticed, however, that the strength of the 2.4 eV band is temperature dependent as well as \( F^- \)-center and \( \text{H}^- \) concentration dependent [77]. Typically, neutron irradiation produces mainly \( F^+ \)-centers while electron irradiation or additive colorization induces mainly \( F^- \)-centers [34]. Rinke et al. argue that given the fact that the position of the absorption band for the \( F \) and \( F^+ \) centers are almost identical, it is to be expected that this is also the case for the emission. Even though similar luminescence peaks for these centers have been predicted in Ref. [40], no substructure in the emission band can be observed experimentally (unlike in the absorption band).

Here, we propose a different interpretation of this observation. We suggest that the \( F^- \)-center does not in fact luminesce. Indeed, modern theoretical computations seem to agree on the fact that the 2.4 eV band does not belong to the \( F^- \)-center luminescence process. We stress that all theoretical results for the emission energy summarized in Table II range from 3.4 eV to 4.09 eV. Moreover, there is a strong photoconversion from \( F \) into \( F^+ \)-centers [78], suggesting that before the \( F^- \)-center has a chance to luminesce, a conversion into \( F^+ \) happens followed by an absorption of the \( F^+ \)-center since the absorption band for it is similar to the \( F \)-band. Our calculations show that the excitation energy for the singlet state in the \( F^- \)-center of MgO converges very slowly with respect to the system size, indicating that the optically excited state is significantly more delocalized than the ground state. This could make a photoconversion into \( F^+ \) significantly more likely and therefore corroborates our interpretation.

C. CaO and SrO

Historically, one of the best studied \( F \)-centers in the alkaline earth oxides is the one in CaO [38]. The identification of the \( F \)-center’s charged state is made easier by the fact that, unlike for MgO, the absorption band is different for the \( F \) and \( F^+ \) centers. Furthermore, we note that the lattice constant of CaO is significantly larger than for MgO, which leads to a reduced confinement of the trapped charges and shifts the absorption band to lower energies. Early theoretical and experimental investigations have interpreted the 2.0 eV emission band to be a transition from a spin and orbital triplet \( ^3T_{1u} \) into the ground state singlet \( ^1A_{1g} \) [38, 62, 79]. However, a \( ^1T_{1u} \rightarrow ^1A_{1g} \) transition is also possible at a slightly higher energy. In general, the CaO luminescence mechanism has been found to be a combination of a singleton-singlet and a triplet-singlet transition which are activated at different temperatures [62, 63]. Since the excited triplet state lies slightly below in energy from the excited singlet state, there is a population conversion at temperatures of around 600 K. Namely, at low temperatures up to 300 K one measures a transition at around 1.98 eV, whereas as the temperature increases the excited singlet gets populated and a much more rapid luminescence gets gradually triggered at around 2 eV [62, 63].

Using EE-EOM-CCSD in combination with the outlined extrapolation techniques yields an absorption and emission energy of 3.13 eV and 1.93 eV for the \( F \)-center in CaO, respectively. To the best of our knowledge only one TD-DFT result can be found in literature for this system, predicting an absorption and emission energy of 3.52 eV and 2.1 eV, respectively. Table II also summarizes two different experimental estimates, showing that the EE-EOM-CCSD and TD-DFT@B3LYP calculations agree with experiment to within 0.1 eV and 0.5 eV, respectively. We note again that GW results for the absorption energy obtained for different levels of self-consistency shows a significant variance ranging from 3.2 eV to 3.87 eV and can not be compared directly to experiment due to the neglect of the exciton binding energy. We note that our quantum chemical results have been obtained using periodic boundary conditions, whereas previous calculations have been carried out using a cluster model approach [30, 64].

Finally, we turn to the discussion of the \( F \)-center in SrO. This system exhibits an even larger lattice constant and the absorption and emission energies are shifted to even lower energies compared to MgO and CaO. However, the \( F \)-center in SrO is qualitatively very similar to the CaO case, and the agreement of EE-EOM-CCSD in both cases with experimental values is excellent. To the best of our knowledge, there exist only experimental estimates of the absorption energy with about 2.4 eV, whereas no measurements for the emission band are known to the authors. We report the results for the singlet-triplet absorption \( ^1A_{CC} \rightarrow ^3T \) and triplet-singlet emission \( ^3T \rightarrow ^1A \) in the infinite supercell size limit in
Table II. We hope that this prediction will be verified experimentally in the future.

IV. CONCLUSIONS

In this work we have presented a novel implementation of the UCCSD and EE-EOM-CCSD methods for periodic systems using a plane wave basis set and applied them to the F-center in the alkaline earth oxides MgO, CaO, and SrO. The implementation was tested on molecular systems, and we have verified it by comparing against well established quantum chemistry codes for a number of molecular and atomic systems. Convergence of calculated excitation energies with respect to the basis set and size of the simulation cell is crucial for reliable predictions in periodic systems. We have presented a framework to obtain basis-set and finite-size corrected excitation energies by freezing the number of occupied orbitals in a controlled fashion and extrapolating to the complete basis set and infinite system size limit.

We have calculated EE-EOM-CCSD absorption and emission energies of the F-center in MgO, CaO, and SrO, accounting for finite basis set and system size errors using extrapolation techniques. The obtained results are in good agreement with previous calculations (where available) [30, 40–42, 64] and with experimental data [61]. In addition, a prediction for the emission band of the F-center in SrO has been made. Furthermore, we provide additional evidence for the assignment of the 2.4 eV band in MgO crystals to recombination processes, and we propose a new interpretation of previous results by suggesting that the F-center in MgO does not luminesce. However, further work is needed to clarify the nature of these transitions.

The achieved level of accuracy for the calculated EE-EOM-CCSD absorption and emission energies shows that this method has the potential to significantly expand the scope of currently available ab initio techniques for the study of defects. However, further improvements for the corrections to the finite basis and system size errors are urgently needed to allow for a more extensive and detailed study of defects in solids on the level of EE-EOM-CCSD theory.

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