Unrestricted Hartree–Fock treatment of paramagnetic defect centers in non-magnetic crystals VI

C. Pisani, U. Birkenheuer

Department of Inorganic, Physical and Materials Chemistry, University of Torino, Via Giuria 5, 10125 Torino, Italy

Received 15 November 1995

Abstract

This paper, the sixth in a series devoted to the presentation of the program EMBED, illustrates the generalization of the perturbed-cluster equations to the case of spin-polarized defects, and the incorporation of this additional facility in the EMBED program. Different possibilities are discussed as concerns the preparation of an initial guess for the selected spin-polarized configuration, and it is shown how the program can track a selected spin-orbital with an occupation number determined from the input throughout the SCF cycle. Preliminary data concerning the F-center in LiF and the Mg 1s core hole in an MgO monolayer are provided as examples.

1. Introduction

In the preceding papers of this series [1–5], we presented EMBED, an ab-initio Hartree–Fock (HF) program for the treatment of local defects in crystals. The method is based on the perturbed-cluster (PC) approach: the solution for a molecular cluster surrounding the defect is corrected self-consistently for environmental effects using terms which are derived from the host crystal solution (see Ref. [1] and references therein for details). The current version of this program (EMBED93) is available from the authors [6]. We anticipated our plan to endow EMBED with a number of additional capabilities to make it more flexible and to widen its range of applications [1]. The treatment of open-shell systems by means of the unrestricted Hartree–Fock technique was mentioned as one of the high priority tasks. Spin-polarized centers constitute an important class of local defects in crystals. Among them there are color centers in ionic crystals [7–11], point defect or dislocation related centers in semiconductors [10,12], activated complexes in catalytic reactions at crystalline surfaces [13], and localized core holes in solids [14].

In the present paper we first briefly discuss the modifications which had to be introduced in the PC equations for treating open-shell defects. Then we describe in more detail the way they have been implemented in the EMBED program. Finally, we provide two examples of application of the present extension of the EMBED program concerning the F center (neutral fluorine vacancy) in bulk LiF, and the 1s Mg core hole in an MgO monolayer.

2. Theory

As usual, we shall consider two basis sets, one associated with the cluster which contains the defect (in the following referred to as C), the other with the indented host crystal (denoted by D), and subdivide all representative matrices on the basis of a sub-matrix
blocking scheme into a "local subspace" (containing the three sub-blocks CC, CD, and DC), and an "external subspace" (formed by the sub-block DD only). The fundamental assumption consists in considering the Green function in the external subspace as essentially unchanged with respect to the corresponding one of the unperturbed (or perfect) host system. Since only non-magnetic host crystals are considered here, we must assume, to be consistent, that the spin density is appreciably different from zero only within the local space. In other words, a one-electron spin-orbital associated with a defect which does not have a counterpart of opposite spin must be localized essentially within the cluster region, and the induced spin-polarization must not extend beyond the local zone. This assumption may require large cluster sizes to be adopted, but we are not concerned with this problem here.

For the description of spin-polarized systems, two different schemes can be adopted in the frame of the HF approximation: either a restricted open-shell HF (ROHF) description, or an unrestricted HF (UHF) description of the defect system wave functions. As is well known, only the first choice results in pure spin states, while the UHF determinant, in which two different sets of orbitals are assigned to the two spins, contains components of different total spin. In fact, it turns out that the UHF scheme is a more direct generalization of the RHF treatment EMBED93 is based on than the ROHF scheme. The latter requires some kind of state selection (double or single occupied states) which is based on the orbitals of the system under study. In the FC approach the defect system wave functions, however, are only available in very particular cases, i.e. if they are localized within the cluster region C. Thus we decided to implement the UHF option first, while leaving open the possibility of subsequent implementation of the ROHF option. For instance, the storage mode of the various density and Fock matrices has been organized in such a way that the consequences of the open-shell treatment (two density matrices, one for the total and the other for the spin density, instead of just one RHF density matrix) and those of the unrestricted treatment (two Fock matrices, one for the \( \alpha \) and the other for the \( \beta \) spin) are carefully distinguished in the implementation.

Let us first summarize briefly the general features of an UHF self-consistent field (SCF) procedure. Once a pair of \( \alpha \) and \( \beta \) spin Fock matrices \( F^\alpha \) and \( F^\beta \) is given, the corresponding \( \alpha \) and \( \beta \) spin density matrices \( P^\alpha \) and \( P^\beta \) are determined exactly in the same way as the RHF density matrix is generated from the RHF matrix. That is,

\[
P^\sigma = \Theta (\epsilon_F - F^{\sigma}) \quad , \quad \sigma \in \{\alpha, \beta\} .
\]

(1)

Next the total and spin density matrices are defined as

\[
p^{\text{tot}} = P^\alpha + P^\beta ,
\]

(2)

\[
p^{\text{spin}} = P^\alpha - P^\beta ,
\]

(3)

which are then used to generate the new pair of Fock matrices,

\[
F^{\sigma'} = T + Z + C [ P^{\text{tot}} ] + X [ P^{\text{tot}} ] + j^{\sigma'} X [ P^{\text{spin}} ] \]

\[
= F^{\text{RHF}} + j^{\sigma'} X [ P^{\text{spin}} ] .
\]

(4)

(5)

Here, \( T \), \( Z \), and \( C \) are the matrices of the kinetic energy, the nuclear attraction, and the Coulomb potential, respectively, \( j^{\sigma'} \) is +1 or −1 according to whether \( \sigma = \alpha \) or \( \beta \), and \( X \) is the matrix of the exchange potential, which is given by

\[
X [ P ]_{\nu \mu} = -\frac{1}{2} \sum_{\lambda \kappa} P_{\lambda \kappa} [ \phi_\nu \phi_\lambda | \phi_\mu \phi_\kappa ] .
\]

(6)

The additional term \( X [ P^{\text{spin}} ] \), necessary to build-up the UHF matrices, is exactly the same as the one for the exchange contribution to the RHF matrix, \( X [ P^{\text{tot}} ] \), despite the different type of density matrices the operator \( X \) is applied to. Finally, the total energy of an open-shell system is given by

\[
E_{\text{tot}} = E_{\text{kin}} + E_{\text{nn}} + E_{\text{en}} [ P^{\text{tot}} ] + E_{\text{ce}} [ P^{\text{tot}} ]
\]

\[
+ E_\epsilon [ P^{\text{tot}} ] + E_\epsilon [ P^{\text{spin}} ]
\]

\[
= E^{\text{RHF}} + E_\epsilon [ P^{\text{spin}} ] ,
\]

(7)

(8)

where \( E_{\text{kin}}, E_{\text{nn}}, E_{\text{en}}, \) and \( E_{\text{ce}} \) are the kinetic, nuclear–nuclear repulsion, electron–nuclear attraction and electron–electron repulsion energy, respectively, and \( E_\epsilon \) is the HF exchange energy

\[
E_\epsilon [ P ] = -\frac{1}{4} \sum_{\nu \mu \lambda \kappa} P_{\nu \mu} P_{\lambda \kappa} [ \phi_\nu \phi_\lambda | \phi_\mu \phi_\kappa ]
\]

\[
= \frac{1}{2} \text{Tr} ( P X [ P ] ) .
\]

(9)

(10)

The same functional \( E_\epsilon \) required to compute the RHF total energy is also used to calculate the spin-polarization contribution \( E_\epsilon [ P^{\text{spin}} ] \) to the open-shell total energy.
The procedure to generate the $\alpha$ and $\beta$ spin density matrices of a paramagnetic defect system is the same as the one used (and implemented in EMBED93) for a closed-shell defect system. Hence, the PC equations [1] can essentially be adopted without any modification. We use here the same conventions as in Ref. [1], namely, a basis set of atomic orbitals (AO, denoted by Greek letters) is adopted in the external zone, while the eigenfunctions $|\sigma\rangle$ of the $P_{\sigma\sigma}^\sigma$ matrices (with eigenvalues $e^{(\sigma)}_j$) are used in the $C$ cluster. We then have, for the CD block,
\begin{equation}
P_{CD}^{\sigma} = P_{CD}^{\sigma,\text{cou}} + P_{CD}^{\sigma,\text{est}},
\end{equation}
with
\begin{equation}
P_{\mu\nu}^{\sigma,\text{cou}} = -\sum_{\gamma} Q^{\sigma}_{\mu\gamma}(e^{(\sigma)}_\nu) M^{\text{RHF}}_{\nu\mu}(e^{(\sigma)}_\nu;1)/2 \quad \text{and} \quad (12)
\end{equation}
\begin{equation}
P_{\mu\nu}^{\sigma,\text{est}} = -\sum_{\gamma} S^{\sigma}_{\nu\mu} P_{\nu\mu}^{\text{RHF}}/2.
\end{equation}
Note that, because of the fundamental approximation, the density sub-matrix of the DD block, $P_{DD}$, and the coupling matrix $M_{DD}(e;1)$ are spin-independent. Even if not directly apparent from Eq. (13), this also holds for the overlap contribution $P_{CD}^{\sigma,\text{est}}$ to the CD block of the defect system densities matrices after being back-transformed to the original, spin-independent AO basis set. In fact, the following equation is used to compute this contribution to the density matrix, directly in the AO basis set:
\begin{equation}
P_{CD}^{\sigma,\text{est}} = -S_{CC}^{-1} S_{CD} P_{DD}^{\text{RHF}}/2.
\end{equation}

The additional factor 1/2 in Eq. (12), (13) and (14) takes into account the fact that both $P_{DD}^{\text{RHF}}$ and $M_{RHF}^{\mu\nu}(e;1)$ refer to the perfect host crystal which is assumed to be non-magnetic and therefore is treated within the RHF approximation. As concerns the CC block, we have
\begin{equation}
P_{CC}^{\sigma} = P_{CC}^{\sigma,\text{clu}} + P_{CC}^{\sigma,\text{cou}} + P_{CC}^{\sigma,\text{est}},
\end{equation}
with
\begin{equation}
P_{\mu\nu}^{\sigma,\text{clu}} = \Theta_\delta(e_F - e^{(\sigma)}_\mu) \delta_{\mu\nu},
\end{equation}
\begin{equation}
P_{\mu\nu}^{\sigma,\text{cou}} = N_{\mu\nu}^{\sigma} + N_{\nu\mu}^{\sigma} \quad \text{and}
\end{equation}
\begin{equation}
P_{\mu\nu}^{\sigma,\text{est}} = -\sum_{\gamma} P_{\mu\nu}^{\sigma,\text{est}} S_{\nu\mu}^{\gamma}.
\end{equation}
The $\Theta_\delta$ function in Eq. (16) is a smoothed Heavyside function, whose value changes linearly from 0 to 1 in the interval $[-\delta, +\delta]$ ("security zone"). Usually, a value $\delta = 0.02$ Ha is adopted. Again, the overlap contribution $P_{CC}^{\sigma,\text{est}}$ to the CC block of the density matrices turns out to be spin-independent in the AO basis set, and is evaluated directly as
\begin{equation}
P_{CC}^{\sigma,\text{est}} = -P_{CD}^{\sigma,\text{est}} S_{CD} S_{CC}^{-1}.
\end{equation}
Finally, the spin-dependent auxiliary matrices $N_{\mu\nu}^{\sigma}$ are either computed as
\begin{equation}
N_{\mu\nu}^{\sigma} = -\sum_{\mu} P_{\mu\mu}^{\sigma,\text{cou}} Q_{\mu\nu}^{\sigma}(e^{(\sigma)}_\nu)/(e^{(\sigma)}_\nu - e^{(\sigma)}_\mu)
\end{equation}
or according to
\begin{equation}
N_{\mu\nu}^{\sigma} = -\sum_{\mu} P_{\mu\mu}^{\sigma,\text{aux}} Q_{\mu\nu}^{\sigma}(e^{(\sigma)}_\nu)/2 - \sum_{\mu} P_{\mu\mu}^{\sigma,\text{cou}} S_{\mu\nu},
\end{equation}
with
\begin{equation}
P_{\mu\nu}^{\sigma,\text{aux}} = -\sum_{\gamma} Q_{\mu\nu}^{\sigma}(e^{(\sigma)}_\nu) M_{\nu\mu}^{\text{RHF}}(e^{(\sigma)}_\nu;2)/2.
\end{equation}
depending on the separation of the two eigenvalues $e^{(\sigma)}_\nu$ and $e^{(\sigma)}_\mu$ involved (for details, see [1]).

Eqs. (11)–(22) apparently are a straightforward extension of the standard PC scheme. However, in their application to some concrete physical problem, two new features come into play, both of which are related to the open-shell structure of the system to be investigated. The first one is the choice and preparation of the proper open-shell state. In many cases the open-shell solution of interest may nor be the ground state of the system, and even if so, as in bond breaking processes with radical intermediates, the question is how to introduce and keep the spin-polarization of this state during the SCF procedure. The second problem concerns the treatment of those coupling contributions to the density matrices which are due to localized states of the defect system.

When studying defects in extended systems, the choice of an appropriate HF configuration is a rather delicate problem. On the one hand, since the defect is coupled to an infinite host, the Fermi statistics of the latter must be obeyed. This means that the occupation number of non-localized HF orbitals is uniquely determined by the Fermi level $e_F$ of the perfect crystal. On the other hand, if the energy level of a given localized defect state system happens to fall into the band gap of a semiconductor or insulator, it may be given any occupation number. In addition, if excited states like
localized core holes are investigated, their occupancy may differ from that dictated by the Fermi statistics, even if they do not belong to the fundamental gap of the perfect host crystal. Hence, in general, the $\alpha$ and $\beta$ spin density matrices of an extended system with a defect center are given by

$$P_{ij}^{\alpha} = \int_{-\infty}^{\infty} \Theta_{\delta}(\epsilon_F - \epsilon) \epsilon_i^{\alpha,\text{deloc}}(\epsilon) \, d\epsilon$$

$$+ \sum_j \epsilon_j^{\alpha,\text{loc}} n_j^{\alpha}(c_{ij}^{\alpha,\text{loc}})^* .$$

with any suitably chosen occupation numbers $n_j^{\alpha}$ for each of the localized states. The PC equations, on the other hand, are based on an integral representation of the density matrices similar to that in Eq. (23) to ensure the correct occupation of the delocalized defect system states. As a consequence, the following “default” setting of the occupation numbers $n_j^{\alpha}$ is adopted by the PC equations,

$$n_j^{\alpha} = \Theta_{\delta}(\epsilon_F - \epsilon_j^{\alpha}) .$$

For some applications (see the example of the neutral F-center in LiF below) the configuration of the defect to be investigated may simply be selected by a proper choice of the Fermi level inside the band gap. A special option has therefore been implemented in the current version of EMBED that allows the Fermi level to be pinned to a certain selected state inside the band gap (for details see Section 3.2).

Other applications, like core hole excitations, require a more severe modification of the PC scheme. A prerequisite for specifying a defect system configuration different from the “default” one just described, is the selection of some individual localized states. In general, no information about the defect system orbitals is generated within the PC scheme: the $|j\sigma\rangle$ eigenstates of the cluster region C are just mathematical intermediates without any direct physical meaning. The case, however, is different for those cluster eigenstates which are also eigenfunctions of the defect system, that is, which not only obey

$$F_{CC}^{\alpha}|j\sigma\rangle = e_j^{\alpha} S_{CC}|j\sigma\rangle ,$$

but also

$$F_{DC}^{\alpha}|j\sigma\rangle = e_j^{\alpha} S_{DC}|j\sigma\rangle .$$

The coupling contribution of these states to the density matrices vanishes, and an alternative configuration may be chosen by setting

$$p_{jk}^{\alpha,\text{clu}} = n_j^{\alpha} \delta_{jk} ,$$

instead of Eq. (16). We therefore have implemented in EMBED an option that enables the cluster contribution to the $\alpha$ and $\beta$ spin density matrices of the defect system to be modified according to Eq. (28) (see Section 3.2 for details).

Still, there is another interesting class of open-shell defects that can hardly be prepared by some state selection during the SCF procedure. These defects are connected to spin-localization effects, as is very likely in bi-radical intermediates of bond breaking processes. Consider the text-book example of the dissociation of an $\text{H}_2$ molecule [15]. The correct ground state for large bond distances is a UHF solution with localized spin orbitals on the two hydrogens atoms, one for the $\alpha$ and the other for the $\beta$ spin. In order to arrive at such a UHF solution one first must reduce the symmetry of the defect system according to the spin-localization (in our example from $D_{\infty h}$ to $C_{\infty v}$). Then an initial spin-polarization must be introduced to the system. In EMBED this can be done either by means of the initial guess for the Fock or density matrices which are obtained as a superposition of atomic plus (indented) perfect crystal sub-matrices or by means of an additional spin-polarizing magnetic field on different fragments of the C cluster during the first few cycles of the SCF procedure. Both options will be described in more detail later (Section 3.2).

3. Computational aspects

3.1. Organization of the SCF procedure

As discussed in Section 2, no new operators or functionals have had to be introduced for the UHF option of EMBED. The spin-dependent exchange contribution $X[P_{\text{spin}}]$ to the Fock matrices as well as the spin-dependent exchange contribution $E_x[P_{\text{spin}}]$ to the total energy of the defect system, or more precisely, to the local energy $E'$ (for details see [1]), were already, at least in principle, embodied in the current version EMBED93. Furthermore, the UHF PC equations differ from the RHF PC essentially only by an additional
index $\sigma$ to distinguish between the $\alpha$ and $\beta$ spin UHF solution.

As is apparent from Eq. (5) and (8), it is much more convenient to deal directly with the total and spin density matrices $P^{\text{tot}}$ and $P^{\text{spin}}$, as well as with the restricted HF operator $E^{\text{RHF}}$ (and energy $E_{\text{RHF}}$), and the spin-dependent exchange contribution $X[P^{\text{spin}}]$ (and $E_s[P^{\text{spin}}]$) to it, than with the corresponding $\alpha$ and $\beta$ spin quantities. Firstly, this scheme is easier to implement. Secondly, it guarantees immediately that in the case of an RHF calculation the results from the current EMBED93 version are reproduced. Thirdly, it is often more efficient to mix the total and the spin density, or their Fock matrix counterparts $F^{\text{RHF}}$ and $X[P^{\text{spin}}]$, instead of the $\alpha$ and $\beta$ components, because it may happen that convergence on the total density is already reached, while the spin-polarization is still changing significantly during the SCF procedure. Only for the application of the PC equations themselves (Eqs. (11)–(22)), are the Fock matrices temporarly transformed into $\alpha$ and $\beta$ spin Fock matrices; the generated $\alpha$ and $\beta$ density matrices are back-transformed into total and spin density matrices immediately afterwards. The resulting program scheme is shown in Table 1. Except for LOWDCU and ATCALD all subroutines of the EMBED program deal with $(P^{\text{tot}}, P^{\text{spin}})$, $(F^{\text{RHF}}, X[P^{\text{spin}}])$ and $(E_{\text{RHF}}, E_s[P^{\text{spin}}])$. Furthermore, all quantities not depending on the electronic charge distribution in the local zone C are computed prior to the proper SCF procedure (from LOWDCU to MIXING).

3.2. Preparation and tracking of selected configurations

There are several different ways of preparing an open-shell configuration for a defect system. They have briefly been summarized in the last part of Section 2 and will be described in more detail in the following:

(a) Initial spin-polarization
This way of preparing an open-shell solution for a defect requires an SCF start from an initial guess built up from a superposition of atomic density or Fock matrices. First, if necessary, the symmetry of the defect surrounding cluster must be reduced according to the envisaged spin-localization. Next, an initial spin-polarization has to be specified.

The spin-polarized atomic solutions of each added atom are used for this purpose with a user supplied orientation ("spin pattern") for each star of added atoms still symmetry related. This initial spin-polarization results in different one-particle eigenstates for the $\alpha$ and $\beta$ spin, and thus may eventually lead to the open-shell solution one is looking for. There is, however, no guarantee to end up with an open-shell configuration this way: it may happen that during the SCF procedure the system simply returns to a closed-shell RHF configuration.

(b) Initial polarization field
An alternative approach to generate an open-shell configuration involving spin-localization consist of superimposing an attractive spin-dependent "localization" potential onto the $\alpha$ and $\beta$ spin Fock matrices according to a user-supplied "spin pattern" for each star of symmetry related atoms in the embedded cluster. In this way, one avoids the necessity of starting the SCF procedure from a superposition of atomic Fock or density matrices which is very useful to study the formation of radicals like CH$_3$ at catalytic surfaces (for an example see [16]). After a few initial SCF cycles the polarizing field is removed, and the system is allowed to reach convergence. Some experience is necessary to decide how strong this additional field must be, and how long it should be turned on to force the defect system into the desired open-shell configuration.

(c) Selected state to pin the Fermi level
Selecting certain localized states of a defect system requires the identification of the state in mind. Thus, a preliminary test calculation, either RHF or UHF, is usually necessary. Once the state which should pin the Fermi level inside the fundamental band gap is found, the irreducible representation (IRREP) it belongs to, and its index within this IRREP, is used to invoke the "Fermi level pinning" option. Care must be taken, however, that these input data coincide with the corresponding ones occurring at the first SCF cycle of the actual EMBED calculation. For this purpose, the EMBED calculation should either be started in the same way as the test calculation, or else by recovering the Fock matrix from the latter one. Correspondingly, the relative index of the selected state must
Table 1
Scheme of the UHF SCF procedure in EMBED

<table>
<thead>
<tr>
<th>ENMADU and ENCALU</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Input:</strong> $p_{\text{tot}}$</td>
</tr>
<tr>
<td><strong>Output:</strong> $E_{\text{est}}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MONCLD and SHECLD/SHEDIR and CHEMPD</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Input:</strong> $p_{\text{tot}}$</td>
</tr>
<tr>
<td><strong>Output:</strong> $P_{\text{RHF,est}}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>XCALCD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Computes the spin independent contribution $P_{\text{SSS}}$ to the density matrices (Eqs. (14) and (19)).</td>
</tr>
<tr>
<td><strong>Input:</strong> $p_{\text{tot}}$, $p_{\text{spin}}$</td>
</tr>
<tr>
<td><strong>Output:</strong> $\rho_{\text{spin}}$, $e_{\uparrow\downarrow}$</td>
</tr>
</tbody>
</table>

IF $\text{INF}(181) > 0$ THEN

<table>
<thead>
<tr>
<th>PATCLD and PSTRTU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generate the initial density matrices according to the spin pattern.</td>
</tr>
<tr>
<td><strong>Input:</strong> $P_{\text{tot}}$, $P_{\text{spin}}$</td>
</tr>
<tr>
<td><strong>Output:</strong> $P_{\text{tot}}$, $P_{\text{spin}}$</td>
</tr>
</tbody>
</table>

ELSE

<table>
<thead>
<tr>
<th>FATCLD and FSTRTU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generate the initial Fock matrices according to the spin pattern or recover the Fock matrices from a previous SCF run.</td>
</tr>
<tr>
<td><strong>Input:</strong> FTM3, (if required)</td>
</tr>
<tr>
<td><strong>Output:</strong> $P_{\text{RHF}}$, $X[p_{\text{spin}}]$</td>
</tr>
</tbody>
</table>

ENDIF

A:

<table>
<thead>
<tr>
<th>LOWDCU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Builds up the $\alpha$ and $\beta$ spin Fock matrices in the symmetry-adapted orthonormal cluster zone basis set.</td>
</tr>
<tr>
<td><strong>Input:</strong> $P_{\text{RHF}}$, $X[p_{\text{spin}}]$, $c_{\alpha \beta}$</td>
</tr>
<tr>
<td><strong>Output:</strong> $F_{\alpha}$, $F_{\beta}$</td>
</tr>
<tr>
<td>Diagonalize the cluster zone Fock matrices $F_{\alpha \beta}$.</td>
</tr>
<tr>
<td><strong>Input:</strong> $F_{\alpha}$, $F_{\beta}$</td>
</tr>
<tr>
<td><strong>Output:</strong> $e_{\alpha \beta}$, $e_{\alpha \beta}$, $e_{\alpha \beta}$</td>
</tr>
</tbody>
</table>

IF convergence on eigenvalues EXIT

<table>
<thead>
<tr>
<th>ATCALD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Builds up the $\alpha$ and $\beta$ spin density matrices according to the UHF PC Eqs. (11) to (22).</td>
</tr>
<tr>
<td><strong>Input:</strong> $p_{\text{tot}}$, $p_{\text{spin}}$</td>
</tr>
<tr>
<td><strong>Output:</strong> $p_{\text{tot}}$, $p_{\text{spin}}$</td>
</tr>
<tr>
<td>Generates the total and spin density matrices in the AO basis set.</td>
</tr>
<tr>
<td><strong>Input:</strong> $p_{\text{tot}}$, $p_{\text{spin}}$</td>
</tr>
<tr>
<td><strong>Output:</strong> $p_{\text{tot}}$, $p_{\text{spin}}$</td>
</tr>
</tbody>
</table>

B:

<table>
<thead>
<tr>
<th>ENESCF and TOTUCL and BIECON/BIEDIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compute the new Fock matrices including the crystal field contribution from the external zone and (if required) the $\nu$-technique perturbation [4].</td>
</tr>
<tr>
<td><strong>Input:</strong> $P_{\text{RHF,est}}$, $p_{\text{tot}}$, $p_{\text{spin}}$</td>
</tr>
<tr>
<td><strong>Output:</strong> $E_{\text{est}}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MIXING</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixes the Fock matrices from the previous cycle (if exists) with the ones of the current cycle.</td>
</tr>
<tr>
<td><strong>Input:</strong> $E_{\text{est}}$, $E_{\text{est}}$, $p_{\text{tot}}$, $p_{\text{spin}}$</td>
</tr>
<tr>
<td><strong>Output:</strong> $E_{\text{est}}$</td>
</tr>
</tbody>
</table>

then be the one of the first, or of the final SCF cycle of the test calculation, respectively. At each cycle of the SCF procedure the state $|j^{\alpha \beta} \sigma\rangle$ in question and its level $e_{\rho \sigma}^{\alpha \beta}$ are identified after diagonalizing the cluster Fock matrix, and the Fermi level is positioned at $e_{\rho \sigma}^{\alpha \beta} \pm \delta$ depending on whether the state is an empty or an occupied one. That means, the Fermi level is chosen in such a way that the
selected state pinning it is at the bottom of the security zone (see Eq. (16)) if occupied, and at the top of the security zone if unoccupied.

In general, selecting a certain spin state to pin the Fermi level is only useful if there already exists a spin-polarization in the electronic structure of the system and hence different $\alpha$ and $\beta$ spin spectra in the cluster zone $C$. This may be achieved either by combining the Fermi level pinning scheme with the initial spin pattern or polarization field option (see items (a) and (b)), or by starting with a Fock matrix from a previous UHF run. Nevertheless, it is also possible to activate the Fermi level pinning option starting from a closed shell RHF configuration. In this unique case, the program automatically assigns in the first SCF cycle the opposite occupation to the partner state of the spin state which has been selected to pin the Fermi level. For example, if an occupied $\alpha$ spin state should pin the Fermi level, the corresponding $\beta$ spin state will be kept empty in the first SCF cycle, although its energy level is lower than the pinned Fermi level. As a consequence, this $\beta$ level will shift upward with respect to the $\alpha$ one, and become progressively less occupied during the SCF procedure, until it leaves the security zone around $\varepsilon_F$ and becomes vacant.

(d) Selected states with occupation not following the Aufbau principle

A different occupation with respect to that dictated by Fermi statistics may be assigned to any localized state using a procedure similar to the Fermi level pinning option just described. Indeed, the same EMBED input data and selection criteria (IRREP, relative index, spin) are used for this purpose. Still, this option differs in some important respects from the previous one:

(i) The selected states must be well localized to justify their non-standard occupation. It is the user who must check if this really is the case. To assist him, EMBED computes (and prints) the total charge connected to the coupling contribution $P_{\mu}^{\sigma, \text{cou}}$ and $P_{jk}^{\sigma, \text{cou}}$ of the selected state, which should be zero if Eq. (27) were strictly observed.

(ii) To be consistent with the assumption of a purely localized state, this contribution, however, is not added to the $\alpha$ and $\beta$ spin density matrices. In principle, this leads to a violation of charge conservation, but keeping this term would open a channel for refilling the empty core state via coupling to the surrounding host. In any event, the effect of this slight charge unbalance on the energy is taken into account through the chemical potential correction $[4]$.

(iii) No Fermi level adjustment is connected with selected states, and thus any localized state may be selected and any occupation may be assigned to it.

Both options, Fermi level pinning and non-standard occupation, may be combined in one SCF run, but of course only one state is allowed to fix the Fermi level.

(c) Tracking selected states

In general, energy levels and the corresponding spin orbitals may change their relative position during the SCF procedure. The most common way of keeping track of a selected spin orbital during an SCF procedure is to use a “maximum overlap” criterion between the corresponding eigenstate at a given SCF cycle and those at the subsequent SCF cycle. In detail, if $c_{\nu \sigma}^\text{ref}$ are the common contra-variant orbital coefficients of a selected state $|j^{\text{sel}}\sigma\rangle$, that is,

$$|j^{\text{sel}}\sigma\rangle = \sum_\nu |\phi_\nu\rangle c_{\nu \sigma}^\text{ref},$$

then we compute and store the co-variant coefficients,

$$\tilde{c}_{\nu \sigma}^\text{ref} = \sum_\mu S_{\nu \mu} c_{\mu \sigma}^\text{ref},$$

of this selected state. In the following SCF cycle the overlap between the previous selected states $|j^{\text{sel}}\sigma\rangle$ and each of the new cluster zone eigenfunction $|k\sigma\rangle_{\text{new}}$ (with contra-variant orbital coefficients $c_{\mu k}^{\text{ref}, \text{new}}$) may then simply be calculated by

$$\langle j^{\text{sel}}\sigma |k\sigma\rangle_{\text{new}} = \sum_\nu \tilde{c}_{\nu \sigma}^\text{ref} c_{\nu k}^{\text{ref}, \text{new}}.$$  

The eigenfunction with maximum overlap is chosen as the new selected state, and its relative index is updated correspondingly.
3.3. Analysis of SCF results

A couple of new analysis tools has been added to EMBED to investigate the electronic structure of the defect system in more detail, especially the effects related to spin-polarization and UHF spin orbitals. First, the output of EMBED has been extended to give the individual spectra of the cluster zone sub-block $F^{\sigma}_{CC}$ of the UHF $\alpha$ and $\beta$ spin Fock matrices, as well as the total and spin charge on subsequent stars of symmetry related atoms in the cluster and the external zones C and D. Both types of information are useful to follow physical trends in the electronic structure going on during the SCF process. In addition, as already mentioned at the end of Section 2, the electronic charge connected to the coupling contribution of each selected states is given in the output to check the assumption of localization of these states. Furthermore, the concept of arbitrary cluster fragments has been introduced into EMBED. By specifying a set of symmetry related atoms of the embedded cluster the user may define any suitable sub-space of the cluster zone C. This subdivision into fragments, if defined, is then automatically used to get additional information about the chemical character of selected states by means of a Mulliken population analysis applied to these states in each SCF cycle. Moreover, at the end of the SCF procedure, a fragment population analysis [17] is performed for the total and the spin density matrix (if it exists) of the complete defect system. Net and gross populations of the individual fragments and the entire sub-spaces C and D, as well as the overlap population between each of these fragments, is printed in the form of a charge and bond order matrix.

The property part of EMBED has been extended, too. The detailed Mulliken population analysis of the various contributions $P_{CC}$, $P_{C(C+D)}$, $P_{C(C+D)}$ and $P_{DD}$ to the complete density matrix of the defect system may now be applied to the total and the spin density separately. Furthermore, there is the possibility of plotting the electron distribution connected to each of these contributions to the density matrices, either along any user specified direction, or in any arbitrary 2-dimensional plane. The perfect host crystal charge density and a charge density built up by superimposing individual atomic densities of an atomic array equal to that of the defect system can also be generated. All these density plots are available as total density and as spin-density maps, except for the electron distribution of the perfect host crystal, which is described at the closed-shell RHF level of approximation. Finally, any of the spin eigenfunctions of the cluster zone Fock matrices $F^{\sigma}_{CC}$ and $F^{\beta}_{CC}$ may be plotted along any 1- and 2-dimensional subsection of real space. Some of these plotting features are illustrated in the examples of application given in the next section.

4. Examples of application

4.1. F-center in LiF

The simplest, and perhaps the most well studied of all paramagnetic defects in crystals is the F-center in alkali halides, corresponding to an electron trapped in an anion vacancy. The F-center is neutral, but it may give rise to a positively charged $\alpha$-center by losing its electron, and leaving an empty ion vacancy. The case of bulk lithium fluoride is considered here. The formation of these defects can be described formally by the two reactions:

\[ \text{I} \quad \text{LiF} + e^- \rightarrow \text{LiF}[F^- : e^-] + F^- \quad (\text{F-center}) \]

\[ \text{II} \quad \text{LiF} \rightarrow \text{LiF}[F^- : \nu^-] + F^- \quad (\alpha\text{-center}) \]

In principle, reaction II is not of interest for our purpose of documenting the new open shell facility because only singlet states are involved. However, the corresponding data is used as an intermediate in the process of identifying and characterizing the F defect (step (d) below). The basis set adopted for the two ions is of triple-zeta quality, and is the same as used in previous studies of defects in bulk or at the surface of LiF [18], and in the test case 2 of Ref. [1]. In all calculations concerning systems with a fluorine ion removed, a ghost atom (zero nuclear charge) is placed in the center of the vacancy which holds the same basis set as the vacant F$^-$ ion. This choice permits us to describe rather accurately the trapped electron (if any), and to eliminate from the start the problem of the basis set superposition error [19]. The standard cluster size chosen for the present computations corresponded to the inclusion of three stars of symmetry related atoms: the central fluorine (or the ghost atom), its six next neighbor lithiums, and its twelve second neighbor fluorines. According to the EMBED nomenclature, (003) or (113) calculations had to be performed for self-embedding and defect calculations.
respectively. The sequence of calculations was as follows:

(a) Run a CRYS TAL calculation for bulk LiF [20]. The resulting main gap is comprised between $-0.5127$ and $+0.2953$ Ha, and the standard value assigned to the Fermi level is $-0.1087$ Ha, the center of the gap. For the subsequent EMBED calculations, the projected densities of states of each band were approximated with polynomials of order 5 or less.

(b) Perform a self-embedding (003) calculation to determine the reference local energy and net charge.

(c) Determine the chemical potential $\mu$ using the v-technique which in the present case results in a value of $1.0445$ Ha/|e|, appreciably less than for the cluster of the corresponding chemical composition in a LiF monolayer (about $1.25$ Ha/|e|) [4].

(d) Substitute a ghost atom for the fluorine ion and perform a (113) RHF calculation, by leaving the Fermi energy at its standard value. The converged solution describes the $\alpha$-center, and, most likely, the state closest to the one of the trapped electron in the F-center will be the lowest unoccupied level in the main gap. This level at $-0.009$ Ha turns out to be the fifth level of $A_{1g}$ symmetry in the order of increasing energy.

(e) Perform a (113) UHF calculation, using as a starting guess the Fock matrix generated at the end of the previous RHF computation. The Fermi level is pinned to the fifth level of the $A_{1g}$ representation, and $\alpha$ spin occupation of this state is imposed. As discussed in Section 3.2 (item b)) this $\alpha$ level (and the Fermi energy) progressively becomes more stable in the course of the SCF procedure, to end up at $-0.157$ Ha (see Fig. 1). The associated $\beta$ state, on the other hand, which is initially forced to be unoccupied, is rapidly destabilized. After only two cycles it rises beyond the safety zone around the Fermi level (whose width is 0.04 Ha), and ends up at $+0.180$ Ha (Fig. 1).

(f) Perform an analysis of the results, by running the PROPEMB part of the program.

This is just the beginning of a serious study for the characterization of the F-center and of the associated $\alpha$-center. In particular, the relaxation of lithium atoms around the two types of defect should be considered, which may require larger clusters to be used, and which should give appreciable effects, especially in the case of the charged $\alpha$-center. Excited states are another interesting issue which can be explored. The results of a more complete study will be described elsewhere. Here, we limit ourselves to illustration of some aspects of direct computational interest.

The knowledge of the major changes in the one-particle spectra connected to the formation of the $F^-$ vacancy and the trapping of the $\alpha$ spin electron is essential in setting up an F-center investigation with EMBED. They are summarized in Fig. 1 which reports the cluster eigenvalues for the three computations described above as item (b), (d) and (e). For comparison, the top valence band and the two lowest conduction bands of the host crystal are also shown, the former being essentially related to $2p$-electrons on the fluorine atoms. The self-embedded cluster closely reproduces the band structure of the perfect LiF host. There are altogether 39 electron levels (including the degeneracy) between $-0.7$ and $-0.5$ Ha which correspond exactly to the 39 $2p$ orbitals of the 13 $F^-$ ions in the embedded (003) cluster. The remaining one-electron energy levels (in the energy range $[-1.0, +2.0]$ Ha of Fig. 1) essentially cover the conduction bands of the perfect LiF host crystal, and even the band gap near $+1.2$ Ha is discernible in the one-particle spectra of the embedded cluster (around $+1.0$ Ha). The creation of the positively charged defect (\alpha-center) causes the three central fluorine $2p$ orbitals which belong to the $T_{1g}$ representation (fourth column of energy levels) to disappear from the valence band (see Fig. 1), and all other levels to be shifted downwards by roughly 0.1 Ha. In particular, one of the totally symmetric states (second column of energy levels) from the conduction band is strongly stabilized, and comes close to the initial Fermi energy of $-0.1087$ Ha (see item (a) above). We have chosen this state, the $5A_{1g}$ one of the embedded cluster, for pinning the Fermi level $E_F$ in the open-shell F-center calculation. The removal of the spin degeneracy of this level as imposed by the RHF scheme causes a very large energy splitting of the corresponding $\alpha$ and $\beta$ levels (by about $\pm0.2$ Ha). All other features of the F-center spectrum, on the other hand, closely resemble those of the corresponding self-embedded cluster calculation, except for the three missing central fluorine $2p$ orbitals, as would be expected since both systems are neutral.
Fig. 1. One particle spectra of the embedded \((n,n',3)\) cluster in bulk LiF. From left to right, the eigenvalues of the unperturbed system (self-embedding), those for the charged \(\alpha\)-center, and those for \(\alpha\) and \(\beta\) spin electrons in the uncharged F-center are reported. For comparison, the top valence band and bottom conduction band of the host crystal are given in the leftmost plot. In each plot the eigenvalues are divided by IRREPs according to the order of their appearance in the EMBED program, that is, from left to right: \(E_g, A_{1g}, T_{2u}, T_{1u}, T_{2e}, T_{1e}, A_{2g}, E_u, A_{2u}\) (note that the \(A_{1u}\) IRREP is not represented among the cluster eigenfunctions). Double and triple degenerate levels are identified by attaching one and two small bars, respectively, to the horizontal line which marks the position of the level. The thin horizontal line marks the Fermi level. Note the change of its position in the F-center calculation.

Table 2
Computational data and results for the three types of calculations concerning bulk LiF: self-embedding, charged fluorine vacancy (\(\alpha\)-center), and neutral fluorine vacancy (F-center). The timings of the SCF part are split into the construction of the density matrices including the diagonalization of the Fock matrices \(((j\tau)+P)\)/cycle) and the setup of the new Fock matrices together with the computation of the local energy \((F+E)\)/cycle). The meaning of the various quantities are: the chemical potential \(\mu\), the local energy \(E'\), the net charge \(q^{\text{net}}\), and the charge-balance corrected energy \(E^{\text{loc}}\) of the embedded cluster. \(q^{\text{def}}\) is the formal charge of the defect.

<table>
<thead>
<tr>
<th>Type of calculation</th>
<th>Self-embedding</th>
<th>(\alpha)-center</th>
<th>F-center</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPU Times (HP730 sec)</td>
<td>RHF</td>
<td>RHF</td>
<td>UHF</td>
</tr>
<tr>
<td>Integrals</td>
<td>590</td>
<td>590</td>
<td>605</td>
</tr>
<tr>
<td>((j\tau)+P)/cycle</td>
<td>23</td>
<td>23</td>
<td>46</td>
</tr>
<tr>
<td>((F+E))/cycle</td>
<td>153</td>
<td>151</td>
<td>159</td>
</tr>
<tr>
<td>Number of cycles</td>
<td>21</td>
<td>35</td>
<td>36</td>
</tr>
<tr>
<td>Total</td>
<td>4575</td>
<td>6983</td>
<td>8285</td>
</tr>
<tr>
<td>Results</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\mu) (Ha/(e))</td>
<td>1.0445</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(E') (Ha)</td>
<td>-1342.5566</td>
<td>-1243.5763</td>
<td>-1242.9201</td>
</tr>
<tr>
<td>(q^{\text{net}}) ((e))</td>
<td>0.0223</td>
<td>0.2462</td>
<td>0.0244</td>
</tr>
<tr>
<td>(q^{\text{def}}) ((e))</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>(E^{\text{loc}}) (Ha)</td>
<td>-1342.5799</td>
<td>-1242.7890</td>
<td>-1242.9456</td>
</tr>
</tbody>
</table>

Table 2 provides some data concerning the computational demands and results of the three different calculations discussed above. In all cases, “very good” computational tolerances (TOL: 5 5 5 5 7 9) were adopted [1]. As a consequence, the number of two-electron integrals to be calculated (86 million) and stored (53 million), and the number of symmetry unique matrix elements of the Fock and density matrix
to be self-consistently determined (2243 and 4486 in RHF and UHF calculations, respectively) were rather large. In all these tests we used the Aitken acceleration scheme [21] with very good performance. The number of SCF cycles needed to reach convergence was less than half that required with the standard “mixing” procedure. This aspect is very important especially when using workstations, because, as is apparent from Table 2, most of the time is spent in the SCF process in this case. Also note that the UHF times practically coincide with the RHF ones, except for the reconstruction of the density matrix (F matrix diagonalization and calculation of $P^{\text{cou}}$) which requires about twice as much CPU time. Also reported in Table 2 are the net charges and local energies, both uncorrected ($E'$) and charge-balance corrected ($E^\text{Qcor}$) [4]. By using the latter values, and the HF energy of an isolated F$^-$ ion obtained with the same basis set, $-99.40726$ Ha, the defect formation energies $E_\text{tot}(\text{defect}) + E_\text{tot}(F^-) - E_\text{tot}(\text{LiF})$ for reactions I and II amount to 6.18 and 10.44 eV, respectively.

The latter value, however, depends on the position of the zero Hartree potential $V^{\text{b0}}$ in the bulk with respect to, let’s say, the top of the valence band as internally chosen by the CRYSTAL program [22] which is arbitrary to a large extent. A more reasonable zero would correspond to the potential $V^{\infty}$ at infinite distance above a (001) surface of LiF. The difference between these two zeros, $\Delta = V^{\infty} - V^{\text{b0}}$, can be estimated by comparing the position of corresponding core levels in the bulk and at the interior of a thick (001) slab,

$$
\Delta = V^{\infty} - V^{\text{b0}} \approx \varepsilon^{\text{slab,int}} - \varepsilon^{\text{bulk}}.
$$

(32)

The associated change in the defect formation energy is $-\Delta \cdot q^{\text{for}}$, because adding $\Delta$ to the Hartree potential of the host crystal changes the total energy of a charged defect system by $-\Delta \cdot q^{\text{for}}$, where $q^{\text{for}}$ is the formal electronic net charge of the defect system. In the present case we took as a reference core level the $1s$ level of fluorine in bulk and at the center of a 5-layer (001) slab, resulting in a shift $\Delta$ of $-0.14$ eV. Using this new reference Hartree potential, the defect formation energy of the $\alpha$-center (reaction II) becomes 10.58 eV.

An illustrative way of visualizing the trapped electron state in the F-center is provided by density and spin density maps. Fig. 2 shows such density maps for the total density of bulk LiF, as well as the $\alpha$- and F-center therein, the former ones given for the sake of reference only. The creation of the fluorine vacancy is discernible as a local minimum in the total charge density of the $\alpha$-center at the site of the vacant anion. With respect to the charged RHF vacancy, the UHF solution which describes the F-center is clearly distinguished. The lone $\alpha$ electron seems to be localized within the octahedron of neighboring lithium ions around the vacancy, resulting in a flat maximum in the total charge distribution at the center of the vacancy. These features are more clearly visible in the spin density map in the right bottom plot. The spin charge distribution which is mainly associated with the trapped electron is essentially localized inside the Li octahedron. In addition, some spin-polarization associated with Pauli repulsion effects is found on the surrounding lithium and fluorine ions of the embedded cluster. An alternative representation of the spin density of the F-defect is given in Fig. 3 which shows the spin density along the [110] direction through the defect center (the diagonal in Fig. 2). The smooth distribution of the lone
electron around the vacant site is evident. The sharp features near the origin are an artifact due to the basis set chosen, which contains the core functions of the ghost atom. In the same Fig. 3 we have reported the total charge difference between the neutral F-defect and the positively charged defect. Near the defect center this difference practically coincides with the charge density associated with the trapped $\alpha$ electron. When moving to the region around the nearby fluorine atom, polarization effects become predominant, which affect to about an equal extent electrons of both spins.

4.2. Magnesium core hole in MgO

The second example concerns the description of a core hole in a magnesium ion inside an MgO slab. Only the case of a 1$s$ core hole is considered here with the slab reduced to a monolayer. A more complete study will be presented elsewhere. In the following we indicate as Mg$^{2+}$ the magnesium di-cation the core electron should be removed from, and as Mg$^{3+}$ the di-cation after a $\beta$ electron has been removed from its 1$s$ core level.

The choice of a suitable basis set is critical for this type of investigation [14]. On the one hand, the same basis set should be employed for both, Mg$^{2+}$ and Mg$^{3+}$, in order to make energy differences meaningful. On the other hand, the basis set should be flexible enough to describe with equivalent accuracy the two very different electronic configurations involved. Furthermore, since the atom in question belongs to the host crystal, its description should essentially correspond to that adopted for obtaining the solution of the host. Note finally that, in calculations concerning extended systems, the use of very flexible sets may give rise to numerical instabilities [23], apart from the fact that they become more costly. We took as a reference the Mg set used for the host crystal calculations [24], which comprised three $s$-type atomic orbitals (AO) resulting from the contraction of 8, 6 and 1 Gaussian type orbitals (GTO), respectively, and two $p$-type AOs, with 6 and 1 GTOs. The HF energy calculated with this basis set for the isolated Mg$^{2+}$ was $E_0 = -198.82008$ Ha, while that for Mg$^{3+}$ was $-149.51335$ Ha, corresponding to a $\Delta$-SCF 1$s$-core-hole binding energy $\delta = 49.30673$ Ha. Fully uncontracting the 1$s$ AO changed $E_0$ and $\delta$ to $-198.82014$ and 49.22073 Ha, showing that the original contraction scheme was extremely efficient for Mg$^{2+}$, much less so for Mg$^{3+}$. To arrive at a 1$s$ contraction scheme equally well adapted to describe both electronic configurations of the cation, a triple-zeta type of contraction, 6+1+1 GTOs, had to be used. Re-optimizing the contraction scheme then led to $E_0 = -198.82006$ and $\delta = 49.22131$ Ha, very similar to the values obtained with uncontracted 1$s$ orbital. In the next step we fully uncontracted the 2$s$ and 2$p$ AOs. This hardly affected $E_0$ ($-198.82101$ Ha), but resulted in a strong reduction of $\delta$ ($48.95471$ Ha), showing that splitting the 1$s$ AO is not sufficient to obtain a balanced description of electrons in the outer shell for the two cationic configurations, and an even more flexible basis set has to be used. We finally arrived at a basis set in which all primitives of the original basis set were kept, except for the two more diffuse ones, with exponents 0.64294 and 0.4, which were substituted by a single Gaussian with exponent 0.50712, and a contraction scheme that can be described as $[61151(s)+411(p)]$; the corresponding values of $E_0$ and $\delta$ are $-198.80467$ and 48.95925 Ha, respectively, which is about 0.016 and 0.005 Ha higher than the results obtained with the uncontracted basis set. This indicates that a rather balanced description of the two species has been found.

A (114) cluster was adopted for describing the defect region, comprising the central magnesium ion...
where the hole is created, its four first neighbor oxy-
gens, and two additional stars of four magnesium ions
each. The selection technique presented in Section 3.2
(item (d)) is used here for creating the core hole.
With the present choice of the cluster, the 1s level of
the central Mg ion from which the β electron must be
extracted initially is the first one of the totally sym-
metric IRREP \(A_{1g}\), because we start the SCF pro-
dure with a superposition of ionic Fock matrices and
the central cation has a more flexible basis set than
the other ones, resulting in a slightly lower 1s core
level. We imposed the β occupancy of that state to
be zero. During the self-consistency procedure the α
1s state of the central di-cation becomes more con-
tracted, due to the missing Coulomb repulsion of the
β 1s electron, and its energy level is shifted down-
wards. Hence, the β 1s electron experiences a more
effectively shielded nucleus, and becomes more dif-
fuse and energetically less stable. A level crossing of
the empty β 1s state during the SCF procedure is the
consequence. It is tracked correctly by the EMBED
program by means of the overlap technique described
in Section 3.2 (item (e)).

The calculations were less cumbersome than those
of the previous example as concerns the number of
integrals to be calculated (24 million bielectronic in-
tegrals), the size of matrices involved, and the time
required per SCF cycle (28 CPU seconds on HP 730),
but reaching convergence was more difficult; about
a hundred cycles were required with very high mix-
ing factors (around 90%), and the Aitken accelerator
was not as effective as in the previous application.
As usual, all energy data have been corrected for charge
balance, using a calculated μ value of 0.4861 Ha/μ.
The core hole results are as follows (in parentheses, those
for the reference host cluster):

\[
\begin{align*}
q_{\text{net}} & = 0.3889 \quad (0.0020) \quad |e|, \\
q_{\text{for}} & = 1 \quad (0) \quad |e| \quad \text{and} \\
E^\text{Qcor} & = -2055.3445 \quad (-2103.3772) \quad \text{Ha}.
\end{align*}
\]

The vertical excitation energy is 48.0327 Ha, con-
siderably lower than the value of 48.9592 Ha for the
isolated ion. The difference is explained by the Madelung
field which stabilizes the positively charged final state
species Mg\(^{1+}\). Comparison with the 1s core level en-
ergy of \(-48.941\) Ha shows that there also is a signif-
ificant final state relaxation contribution of 0.908 Ha to
the core level binding energy of the Mg 1s state in a

\[\text{MgO}(001)\] monolayer slab.

Fig. 4 reproduces the spin density in the mono-
layer around the core hole. The most important mes-
sage conveyed by this plot in the present context is
that the spin-polarization is very well localized, as ex-
pected, thus confirming the validity of the assumptions
adopted. Also note that there is a slight prevalence of
β with respect to α spin electrons on neighboring oxy-
gens, corresponding to a Mulliken spin population of
\(-0.003 \quad |e|\) on each of these ions. Further interesting
aspects of the calculation are revealed by the plots of
Fig. 5, where the difference between the σ-electron
density in the defective and in the perfect crystal is
reported for both the α and β spin. In the direct prox-
imity of the magnesium nucleus the α spin density is
higher in the defective than in the unperturbed system,
showing that the lone 1s electron comes closer to the
nucleus due to lack of repulsion from the partner β
electron. The absence of the latter is clearly evident,
as well as a general contraction of all other electrons
of the magnesium ion, owing to the higher effective
core charge. Farther away, polarization effects become
the dominant feature, similar to those observed for the
α-center in LiF.
5. Conclusions

The new UHF option enlarges the scope of the program EMBED, by offering the possibility of studying a variety of problems of great interest in research and applications. Two such examples have been given here. However, even more so than in the case of the RHF applications, there is a need for careful and painstaking investigations in order to make this tool fully exploitable: in particular information must be collected, and experience must be gained as concerns the choice of suitable basis sets, the best way to define the spin-polarized states and to achieve convergence, and the correct interpretation of the configuration the defect system finally converges to. A detailed discussion of some of these problems has been given here. As far as we know, the present technique has unique capabilities when effects of the crystalline environment on spin-polarized defects must be taken into account accurately.

Acknowledgements

Financial support from the Italian CNR (Progetto Finalizzato Chimica Fine 2), from the Italian MURST (40%), from the European Community (contract no CHRX-CT93-0155), and from CSP (Centro per il Super calcolo Piemonte) is gratefully acknowledged. The authors are grateful to Irma Scorza for her help in collecting the results described in the present work. U.B. also thanks the Scientific Commission of the NATO for financial support via a post-doc grant of the Deutscher Akademischer Austauschdienst (DAAD).

References


