Density functional theory description of hole-trapping in SiO$_2$: a successful self-interaction-corrected approach.

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We present a self-interaction-corrected (SIC) density-functional-theory (DFT) approach for the description of systems with an unpaired electron or hole such as spin 1/2 defect-centers in solids or radicals. Our functional is easy-to-implement and its minimization does not require additional computational effort with respect to ordinary DFT functionals. In particular it does not present multi-minima, as the conventional SIC functionals. We successfully validate the method studying the hole self-trapping in quartz associated to the Al substitutional impurity. We show that our approach corrects for the well known failures of standard DFT functionals in this system.

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When an electron, a hole, or an electron-hole pair is introduced in an insulator, its wavefunction can have different degrees of localization. It can be localized (self-trapped) on a single atom/bond or it can be delocalized on a larger scale. Trapped electron or hole centers occur in very different systems. The F-centers in alkali halides are paramagnetic centers formed by electron defects trapped on negative ion vacancies in the crystal. They can be obtained by introducing a stoichiometric excess of alkali metal atoms or ionizing the crystal with radiation. Trapped hole defects are found in alkaline earth oxides ([(M]$^0$ centers) upon substitution of the divalent alkaline earth atom with a monovalent one.

Several examples of self-trapping occur in silica. Holes and electrons induced by ionizing radiation self-trap in amorphous SiO$_2$ but not in quartz. In quartz, localization of holes is achieved via the substitution of Si with a trivalent atom (e.g. Al). Similarly, electron self-trapping is obtained substituting a Si with a pentavalent atom (e.g. P). Self-trapped holes or electrons in quartz can also be obtained by substituting Si with Ge and by removing or adding an electron with ionizing radiation. Excitons self-trap both in amorphous Silica and in quartz.

The study of self-trapping of centers in both amorphous and crystalline SiO$_2$ is a subject of important technological implications. The creation of self-trapped centers in SiO$_2$ due to ionizing radiation or high intensity UV light determines the degradation of UV-transmitting fibers (for e.g. UV lithography). Moreover self-trapped defects are partly responsible for the failure rate of MOS devices which use amorphous SiO$_2$ as an insulating layer.

From a theoretical point of view, the description of trapped defects is particularly challenging since a standard density functional theory (DFT) approach based on the local spin density approximations (LSDA) or on its improved version, the spin polarized generalized gradients approximations (SPGGA), often fails to reproduce the localization of the defect wavefunction. Unrestricted Hartree Fock (UHF) calculations usually correctly reproduces the self-trapping. However the UHF description of the defect-free system is usually less accurate than that obtained with DFT. Also, UHF is computationally more demanding.

DFT predicts most F-centers in alkali halides to be delocalized. In the case of SiO$_2$, electron self-trapping is correctly described by DFT, whereas holes are found delocalized. A prototype example are neutral Al centers in SiO$_2$. The structure of pure silica is composed of corner-sharing SiO$_4$ tetrahedrons. The Al doping occurs as a substitution of a Si in the tetrahedral structure, resulting in consequential modifications of electronic and geometric properties. The Al-Si substitution introduces in the system a hole which, according to electron spin resonance, is localized on one of the surrounding oxygen. On the contrary, and in clear disagreement with experimental findings, DFT using standard functionals predicts a hole wavefunction delocalized over the four surrounding oxygens. For this reason the description of hole trapping on Al impurities in Silica has been defined “a challenge for density functional theories”.

As suggested by several authors the failure of DFT in describing self-trapping in general, and self-trapping on Al centers in particular, might be due to the incomplete cancellation of the unpaired-electron self-interaction. This cancellation occurs exactly in UHF. A possible solution to the problem might be to use self-interaction corrected (SIC) functionals. It is indeed well known that SIC functionals can describe electronic states which are not reproduced by LSDA/SPGGA functionals. Unfortunately, the implementation of DFT functionals with self-interaction corrections on each orbital, besides being technically complex, leads to multi-minima problems and sometimes degrades the results obtained with standard functionals.

In this work we show that SIC functionals are indeed a remedy to the failure of DFT in describing Al defects in Silica. We present an easy-to-implement SIC functional for one-particle spin 1/2 defects in solids. In our SIC functional approach we apply the self-interaction correc-
tion to the unpaired electron only. We treat the closed shell system formed by the remaining $2N$ electrons using standard DFT functionals but imposing the conditions that up and down electrons with the same orbital quantum numbers have identical spatial wavefunctions. Our method is free from the multi-minima problem found in previous SIC implementations and its computational cost is equal to that of ordinary DFT functionals. We validate the method against experimental data by calculating optimized geometries and hyperfine coupling parameters of AI defects in silica.

We consider a system of $2N+1$ electrons with $N_\uparrow = N + 1$ up electrons and $N_\downarrow = N$ down electrons. The wavefunction of the $i^{th}$ $\sigma$-electron ($\sigma = \uparrow, \downarrow$) is $|\psi_\sigma_i\rangle$. Throughout the paper we assume the wavefunctions $|\psi_\sigma_i\rangle$ to be orthonormal. We write $n_\sigma(r) = \sum_{\sigma = \uparrow, \downarrow} \sum_i |\langle r | \psi_\sigma_i \rangle|^2$ and $n(r) = \sum_\sigma n_\sigma(r)$. The magnetization density is $m(r) = n_\uparrow(r) - n_\downarrow(r)$.

In spin polarized density functional theory the total energy functional is:

$$F[\{\psi_\sigma\}] = T[\{\psi_\sigma\}] + E_{KS}[n_\uparrow, n_\downarrow] + \sum_{\sigma = \uparrow, \downarrow} \sum_{i,j} \lambda^\sigma_{ij} |\langle \psi_\sigma_i | \psi_\sigma_j \rangle - \delta_{ij}|$$

(1)

where $T[\{\psi_\sigma\}] = -\frac{1}{2}\sum_\sigma \sum_{i,j} N_\sigma \langle \psi_\sigma_i | | \psi_\sigma_j \rangle |\Delta_\sigma|_2$ is the single particle kinetic energy and $E_{KS}[n_\uparrow, n_\downarrow] = E_{ext}[n] + E_H[n] + E_{xc}[n_\uparrow, n_\downarrow]$. The functionals $E_{ext}[n]$, $E_H[n]$ and $E_{xc}[n_\uparrow, n_\downarrow]$ are the external potential and the Hartree and exchange-correlation functionals respectively.

Atomic units are used throughout the paper. Lagrange multipliers $\lambda^\sigma_{ij}$ are included to impose the wavefunction orthonormalization condition. The ground state energy is obtained by minimizing the total energy functional, namely by imposing $\frac{\delta F[\{\psi_\sigma\}]}{\delta \psi_\sigma_i} = 0$, for each $i$ and $\sigma$.

Upon derivation of the total energy functional respect to $|\psi_\sigma\rangle$, we obtain:

$$\frac{\delta F}{\delta |\psi_\sigma\rangle} = \left[ -\frac{\Delta}{2} + V_{KS}(r) \right]|\psi_\sigma\rangle + \sum_{j=1}^{N_\sigma} \lambda^\sigma_{ij} |\psi_\sigma_j\rangle$$

(2)

where $V_{KS}(r) = \frac{\delta E_{KS}[n_\uparrow, n_\downarrow]}{\delta n_\sigma(r)}$.

The Hartree functional $E_H$ in $F[\{\psi_\sigma\}]$ contains a self-interaction term for each electron. If the exact functional is used, these terms are exactly canceled by an identical term (with opposite sign) included in $E_{xc}$. When approximate forms of $E_{xc}$ are used, a self-interaction is introduced in $F[\{\psi_\sigma\}]$, since $E_{xc}$ no longer cancels the self interaction terms in $E_H$ exactly. This self-interaction is unphysical and must be subtracted. Since there is one spurious self-interaction term per electron, the elimination of all the terms leads to an orbital-dependent correction in the functional. The resulting Kohn-Sham equations are not invariant anymore for a unitary transformation in the subspace of occupied orbitals, and the minimization of the functional leads to multi-minima problems. When DFT calculations give a good description of the system without the spin 1/2 center (i.e. pure SiO$_2$) the relevant self-interaction is typically the unpaired electron’s one. As a consequence we propose to subtract the self-interaction only for the unpaired electron. More specifically, we remove only the self-interaction term associated with the magnetization density $m(r)$. Indeed, using standard DFT functionals, the Kohn-Sham eigenstates are such that $|\psi_\uparrow\rangle \approx |\psi_\downarrow\rangle$ and $m(r) \approx \langle r | \psi_{N+1} \rangle^2$ (for which eigenstates we have $\lambda^\sigma_{ij} = \delta_{ij} \epsilon_\sigma$, where $\epsilon_\sigma$ are the Kohn and Sham eigenvalues). As it will be shown below, this strategy eliminates both the orbital dependence of the equations and the multi-minima problem.

A straightforward way to subtract, at least partially, the self-interaction was developed by Perdew and Zunger (SPZ). Applying this approach to the unpaired-electron leads to the definition of a new self-interaction corrected functional (denoted SPZ), $F_{SIC}[\{\psi_\sigma\}] = F[\{\psi_\sigma\}] + \Delta F_{SPZ}[n_\uparrow, n_\downarrow]$, where

$$\Delta F_{SPZ}[n_\uparrow, n_\downarrow] = -E_H[n] - E_{xc}[m,0]$$

(3)

This amounts to subtracting the self-interaction term associated with the magnetization density from both the Hartree and from the exchange correlation functionals.

Besides the SPZ scheme, in this work we propose a new SIC functional (denoted US), defined as $F_{SIC}[\{\psi_\sigma\}] = F[\{\psi_\sigma\}] + \Delta F_{US}$, where

$$\Delta F_{US}[n_\uparrow, n_\downarrow] = -E_H[n] - E_{xc}[n_\uparrow, n_\downarrow] + E_{xc}[n_\uparrow - m, n_\downarrow]$$

(4)

namely, (i) we subtract the unpaired electron self-interaction from the Hartree functional and (ii) we replace the exchange correlation functional for the 2N+1 electrons system with the one for the 2N electrons system without the unpaired electron.

Unfortunately, the US or PZ self-interaction corrected functionals are not sufficient by themselves to obtain physically relevant densities. Due to the quadratic dependence (with a negative sign) of $E_H$ respect to $m(r)$, the two functionals tend to maximize everywhere $|m(r)|$ by separating the spin up and spin down densities. As a consequence $|\psi_\uparrow\rangle$ becomes very different from $|\psi_\downarrow\rangle$ for $i \leq N$ and $m(r)$ is not approximately equal to $|\langle r | \psi_{N+1} \rangle|^2$. This unphysical solution can be eliminated by introducing a second constraint on the 2N-electrons system, i.e. the system without unpaired electron. We impose that up and down electrons with the same orbital quantum numbers have identical spatial wavefunction (spin-restricted solution):

$$|\psi_{i\uparrow}\rangle = |\psi_{i\downarrow}\rangle = |\psi_i\rangle \quad \text{for} \quad i = 1, ..., N$$

$$|\psi_{N+1}\rangle = |\psi_{N+1}\rangle$$

(5)

(6)

In this way the total energy becomes a function of $\{\psi_i\}$:
\[ F_{\text{SIC}}[\{\psi_i\}] = T[\{\psi_i\}] + E_{\text{KS}}[n_\uparrow, n_\downarrow] + \sum_{i,j=1}^{N+1} \eta_{ij} \langle \psi_i | \psi_j \rangle - \delta_{ij} \] (7)

where the \( \eta_{ij} \) Lagrange multipliers are used to enforce the orthonormalization conditions. \( \Delta F_{\text{SIC}}[n_\uparrow, n_\downarrow] \) is the SIC correction in the SPZ (eq. 3) or in the US (eq. 4) scheme. Minimization of the total energy functional can be achieved by imposing \( \frac{\partial F}{\partial \psi_i} = 0 \) for \( i = 1, \ldots, N+1 \). Functional derivation respect to \( \langle \psi_i \rangle \) leads to:

\[ \frac{\delta F_{\text{SIC}}}{\delta \langle \psi_i \rangle} = \frac{\Delta}{2} + V_{\text{SIC}}^T |\psi_{N+1}\rangle + \sum_{j=1}^{N+1} \eta_{N+1j} |\psi_j\rangle \] (8)

\[ \frac{\delta F_{\text{SIC}}}{\delta \langle \psi_i \rangle} = 2 \left[ -\frac{\Delta}{2} + \frac{V_{\text{SIC}}^T + V_{\text{SIC}}^T}{2} \right] |\psi_i\rangle + \sum_{j=1}^{N+1} \eta_{ij} |\psi_j\rangle \] (9)

The potential \( V_{\text{SIC}}^\sigma \) is defined as \( V_{\text{SIC}}^\sigma(r) = V_{\text{KS}}^\sigma(r) + \frac{\delta F_{\text{SIC}}}{\delta n^\sigma(r)} \), where \( \Delta F_{\text{SIC}} = \Delta F_{\text{SPZ}} \) or \( \Delta F_{\text{US}} \) depending on which subtraction scheme is adopted (eq. 3 or eq. 4).

Equations 8 and 9 form a set of self-consistent equations coupled via the terms involving Lagrange multipliers. The condition of \( \frac{\partial F}{\partial \psi_i} = 0 \) is equivalent to the minimization of the corresponding functional. For fixed ionic positions we minimize the SPZ and US functionals with the constraints in eq. 6 using the the gradients given in eq. 8 and the Car-Parrinello 14, 15 method with a damped molecular dynamics approach 16. We used combined electronic and ionic dynamics for the geometry optimizations.

We simulate the structure of an Al defect in Silica using a neutral cell of 72 atoms (one Al atom, 23 Si and 48 O). We perform electronic structure calculations 15, 17 using DFT in the spin polarized generalized gradient approximation and the Perdew-Burke-Ernzerhof (PBE) functional 15 corrected for self-interaction in eq. 3 and in eq. 4. We use norm conserving pseudo-potentials 19. The wave functions are expanded in plane waves using a 70 Ry cutoff. We sample the Brillouin zone with the \( \Gamma \) point and we impose the \( \langle \tau | \psi_i \rangle \) to be real 21.

The results of geometrical optimization using different functionals are illustrated in tables II and III. We label \textit{delocalized geometry} a structure in which the hole wavefunction is delocalized on the four O atoms surrounding the Al one. On the contrary a \textit{localized geometry} is a structure in which the hole wavefunction is localized on one of the four surrounding Oxygens. For a given functional we indicate the structure corresponding to an absolute minimum with \textit{stable} and to a local minimum (but not the absolute one) with \textit{metastable}. The structure not corresponding to any minimum is called \textit{unstable}. The PBE stable structure 6 is a delocalized geometry, in qualitative disagreement with UHF. The SPZ stable structure is delocalized. However a metastable localized solution occurs at slightly higher energy (1.3 mRyd). The US stable structure is localized, in agreement with the UHF results. We did not find any metastable solution using the US functional and in particular the delocalized structures found with PBE or SPZ are unstable. Finally, to judge the effects of the spin-restricted prescription, we compute the total energy difference between the localized and the delocalized structures using PBE with the constraint of eqs. 5 and 6. We obtain 45.6 mRyd which is very close to the unrestricted Hartree-Fock and density functional theory with functionals PBE 13, SPZ and US.

| Functional  | Localized geometry | Localized geometry |
|-------------|--------------------|--------------------|
| PBE         | stable             | unstable (43.9 mRy) |
| SPZ         | stable             | metastable (1.3 mRy) |
| US          | unstable (238 mRy) | stable             |
| UHF         | unknown            | stable             |

\begin{table}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Bond & PBE[18] & SPZ & SPZ & US & UHF[6] \\
\hline
Al-O(1) & 1.744 & 1.742 & 1.938 & 1.957 & 1.924 \\
Al-O(2) & 1.744 & 1.742 & 1.713 & 1.710 & 1.688 \\
Al-O(3) & 1.753 & 1.748 & 1.706 & 1.705 & 1.703 \\
Al-O(4) & 1.753 & 1.748 & 1.719 & 1.715 & 1.689 \\
Si-O(1) & 1.613 & 1.596 & 1.756 & 1.793 & - \\
Si-O(2) & 1.613 & 1.596 & 1.604 & 1.602 & - \\
Si-O(3) & 1.618 & 1.595 & 1.595 & 1.595 & - \\
Si-O(4) & 1.618 & 1.595 & 1.601 & 1.601 & - \\
\hline
\end{tabular}
\end{table}

\textbf{TABLE II:} Bond-lengths (Å) around the substitutional Al impurity using unrestricted Hartree-Fock and density functional theory with functionals PBE[18], SPZ and US.
with UHF.

| Geom: | PBE | US | SPZ | US | UHF[6] |
|-------|-----|----|-----|----|--------|
|       | -17.0 | -72.9 | -96.9 | -89.5 | -89.3 | -85.0 |
| O(1)  | 8.46 | 36.3 | 48.3 | 44.6 | 44.6 | 41.2 |
|       | 8.55 | 36.7 | 48.6 | 44.8 | 44.7 | 43.8 |

TABLE III: Anisotropic hyperfine parameters (Gauss) of the $^{17}$O (1) atom. The first row “Geom:” indicates the functional used to determine the geometry, the second row “Fun:” the functional used in the hyperfine coupling calculation. In this table SPZ geometry refers to the metastable localized structure obtained with the SPZ functional (see text).

To validate our SIC methods against experiment we compute hyperfine parameters using the formalism developed in ref. [21]. The hyperfine interaction includes an isotropic part (Fermi contact) and an anisotropic (dipolar) part. The isotropic part measures the spin density at the nucleus and it is non-zero only for wavefunctions containing s-wave components [21]. The hole state, both in the localized and delocalized solutions, corresponds to the O 2p lone-pair state. Thus the Fermi contact is mainly due to the spin polarization of the doubly occupied O 2s state. Since the spin-restricted conditions (eqs. 5 and 6) suppresses such spin polarization, the Fermi contact term cannot be computed with our spin-restricted SIC functionals [22]. On the other hand, we can access the anisotropic terms since they capture the p-like component of the electron wavefunction which is weakly affected by the spin-restricted condition [22]. In table III we report the principal values of the dipolar part for $^{17}$O atoms. Our implementation of the SIC functional substantially improves the PBE results, giving a dipolar part very close to the UHF results and the experimental data.

In this work we have presented a very effective and easy-to-implement self-interaction corrected approach. It can be applied to hole or electron spin-1/2-centers in solids. We have validate our method by calculating energetics, geometries and hyperfine couplings of neutral Al substitutional defects in quartz. Our SIC approach corrects the known deficiencies of standard DFT functionals and gives results in good agreement with experiments and with the self-interaction free UHF calculations. Thus the functional proposed in this work solves the problem of describing the behavior of hole self-trapping in silica in the framework of density functional theory. Finally we note that our approach can also be applied to molecular systems such as spin 1/2 radicals which represents a fundamental subject of research in chemistry and biochemistry.

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