Orbital coupling in double-vacancy and two-electron systems

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In double-core-hole states where two electrons are removed from different core orbitals, the SCF approach produces artificially low singlet-state energies, leading to energy separations between corresponding singlet and triplet states which can be wrong by orders of magnitude. We present a theoretical analysis of this singlet-triplet separation problem, revealing that the SCF breakdown depends exclusively on the coupling between the core orbitals involved and can be viewed as a particular form of "spin-constrained" variational collapse in the singlet state. The SCF procedure on this state tries to mimic the energetically lower closed-shell singlet ground state even though it has to work with an open-shell configuration. We further prove analytically that it is still possible to obtain reliable estimates of the singlet-triplet splitting in a one-particle picture and show how to construct suitable orbitals. The theoretical analysis is complemented and supported by results on SiX₂⁺ (X = H, F) obtained by a propagator method, as well as a full treatment of the related two-electron system Si¹⁺.

1. Introduction

Quite recently, attention has been paid to the creation of double and multiple vacancies in the cores of atoms [1-3] and molecules [4-9]. Some theoretical studies on double-core-vacancy states have been carried out, yielding the first valuable experience on the theoretical treatment of these interesting species [6-9]. One problem in the application of the SCF procedure to these excited states of double-vacancy systems is that the iterations tend to collapse variationally onto lower-lying states [6,9]. But in addition to this variational collapse, we encounter another general deficiency of the SCF procedure for these systems. The comparison of the SCF results and those obtained by a propagator method has shown that the energies of singlet double vacancies where one electron is removed out of the 1s and one out of the 2s core orbitals are poorly predicted by the SCF procedure, leading to much too small singlet-triplet (S-T) energy splittings [9].

In this work, we intend to answer the question what happens at the SCF level for these singlet states and related cases. We anticipate that the coupling system of two holes is closely related to that of two (unpaired) electrons. This may allow us to carry out a more transparent discussion of the S-T separation problem. While there appears to be a lack of information on this subject for double and multiple vacancies in atomic and molecular systems, a first indication of the S-T separation problem has been reported for two-electron atoms (e.g. the helium atom [10]). We have chosen to study the (1s2s) double vacancies in the Si atom of SiX₂ (X = H, F) as prototypes mainly because of the availability of previous investigations [9]. The two-electron counterpart is Si¹⁺ and its investigation allows us to analyze the coupling of the electrons in the core orbitals of the same atom.

2. Theory and numerical results

As mentioned in section 1, the SCF procedure and the Green function method give grossly different results concerning the splittings of the Si(1s2s) S-T pairs of SiX₂ (X = H, F) [9]. In contrast to the Green function which predicts S-T separations of nearly 11 eV, the SCF calculations yield much smaller splittings of less than 2 eV. The latter figure is typically found for doubly ionized valence states [11-13]. As
a result of our preceding analysis of the S–T separation problem, we can exclude that this strong deviation is an artifact of the not fully "converged" SCF calculations performed, caused by the variational collapse (further details are given in the appendix and ref. [9]).

In the following, we concentrate on the discussion of the S–T separation problem. Guided by the idea that the coupling system of two vacancies shows high analogy to that of two electrons, we study first the related two-electron Si\textsuperscript{12+} in order to gain more insight into the S–T separation problem. This system is, of course, lacking the variational-collapse problem and can be treated at a more accurate computational level, thus enabling us to discuss the S–T separation problem more transparently. In addition, two-electron systems are of interest by themselves.

At the SCF level, the energy \( E^T \) of the triplet state \( \psi^T(1s2s) \) of the 1s and 2s electrons reads

\[
E^T(1s2s) = h_{i1,i2} + h_{2s,2s} + J_{1s,2s} - K_{1s,2s}
\]

where \( h_{i,j} = \langle i|\hat{H}|j\rangle \) (\( i,j = 1s, 2s \)) are the usual one-particle matrix elements and \( J_{i,j} \) and \( K_{i,j} \) denote the Coulomb integral and the corresponding exchange term, respectively. It is known that this energy is invariant to arbitrary rotations within the 1s and 2s orbital space. This invariance can easily be understood when considering that in the triplet state, the 1s and 2s orbitals satisfy the same Fock operator. As a consequence, the energy remains unchanged upon the mixing of these orbitals formally belonging to the same shell.

In the corresponding singlet state \( \psi^S(1s2s) \), we encounter a quite different situation. The first-order energy,

\[
E^S(1s2s) = h_{1s,1s} + h_{2s,2s} + J_{1s,2s} + K_{1s,2s}
\]

changes to

\[
E^S(1s2s) = E^S(1s2s) + A \sin^2 2\theta - B \sin 4\theta
\]

when computed with "new" orbitals 1s and 2s obtained by rotating the "initial" orbitals by an angle \( \theta \). For convenience, we have introduced the abbreviations,

\[
A = \frac{1}{2} (J_{1s,1s} + J_{2s,2s}) - J_{1s,2s} - 2K_{1s,2s}
\]

and

\[
B = V_{2s,1s,1s} - V_{1s,2s,2s}
\]

where, generally,

\[
V_{ijkl} = \langle i(1)|j(2)\rangle |r_1 - r_2|^{-1} |k(1)|l(2)\rangle.
\]

Obviously, the SCF energy of \( \psi^S \) is, in contrast to the energy of the triplet configuration, not invariant to a mixing of the 1s and 2s orbitals. The SCF procedure thus lowers the singlet energy upon this mixing. We now adopt the simple model that the two orbitals 1s and 2s are the only SCF degrees of freedom. As will be shown later, the results of our calculations largely justify this assumption. The rotational angle \( \theta \) that minimizes the energy yields the SCF solution and is simply given by

\[
\tan 4\theta = 2B/A.
\]

At the SCF level, the SCF orbitals 1s and 2s satisfy

\[
V_{1s,1s,1s} = V_{1s,2s,2s} = 0 \quad \text{i.e.}
\]

\[
E^S(1s2s) = E^S(1s2s) + B = 0
\]

\( B \) can thus be seen as the Fock matrix element connecting the 1s and 2s orbitals.

The condition (3a) characterizes the stationary point of the singlet energy as a function of \( \theta \) and we are left with the task to specify the interval of such \( \theta \) representing a minimum of \( E^S \). A straightforward analysis reveals that, if \( A > 0 \) and \( \theta \) is taken to range from \(-\pi/4\) to \(\pi/4\), the solution to eq. (3a) where \(|\theta| < \pi/8\) represents a minimum, while the solution where \(|\theta| > \pi/8\) is a maximum (the sign of \( \theta \) depends only on the relative phase of the orbitals). If \( A < 0 \), the opposite holds true, showing that in the vicinity of a minimum (maximum) \( A \) must be positive (negative). This means that, if the starting value of \( A \) lies sufficiently close to a minimum, then a smaller \(|\theta|\) must yield the exact minimum. For a smaller \(|\theta|\) to be the sought solution, however, it must be that \( A > 0 \).

At the SCF level, the energy lowering,

\[
\Delta E^S = E^S(1s2s) - E^S(1s2s)
\]

\[
= \frac{1}{2} A (1 \pm \sqrt{1+4B^2/A^2})
\]

can be expressed in terms of \( A \) and \( B \) only. The minus (plus) sign stands for \( A > 0 \) (\( A < 0 \)). Of course, eq. (4) shows that all the information concerning the magnitude of the energy lowering is already con-
tained in the matrix elements of the starting orbitals.

The singlet wavefunction \( \psi_1^s \), after the rotation of the initial orbitals by \( \theta \), takes on the following appearance:

\[
\psi_1^s = \cos 2\theta (\psi_1^s) + \frac{1}{\sqrt{2}} \sin 2\theta (\psi_2^s - \psi_3^s).
\]

Expressed in terms of \( A \) and \( B \) after using condition (3a), one finds

\[
\psi_1^s = \frac{1}{\sqrt{2}} \sqrt{1 + C} (\psi_1^s) + \frac{1}{\sqrt{2}} \sqrt{1 - C} (\psi_3^s - \psi_5^s),
\]

where \( C = A/\sqrt{A^2 + 4B^2} \cdot |C| \leq 1 \). This means that, as a result of the 1s/2s orbital mixing, the configurations \( \psi_3^s (1s^2) \) and \( \psi_5^s (2s^2) \) contribute (with equal weights) to the singlet wavefunction. Thus, \( \psi_1^s (1s2s) \) acquires also some character of the energetically higher lying configuration \( \psi_5^s (2s^2) \) which may not be expected a priori in the light of the variational principle. The influence of orbital mixing increases with decreasing \( C \).

At this stage of the discussion it becomes evident through which mechanism the artificial energy lowering of \( \psi_1^s \) takes place at the SCF level. The ground state \( \psi_0^s (1s^2) \) is characterized by a closed-shell determinant, and thus cannot be reached by variational collapse of the SCF procedure on \( \psi_1^s (1s2s) \) because the latter state in an open-shell case. Driven by the variational principle, the SCF procedure artificially mixes the 1s and 2s orbitals in order to mimic as closely as possible the state \( \psi_0^s (1s^2) \) lying at lowest energy.

To support our above analytically derived conclusions, we present, in the following, computational results on the \( \text{Si}^{12+} \) ion. We have first performed an SCF calculation on the \( \psi_1^s \) state of \( \text{Si}^{12+} \). The results confirm to within the accuracy of the calculation the equality of \( V_{28,15,11,15} \) and \( V_{18,25,28,23} \) for the SCF orbitals, and thus the SCF condition (3). Additional SCF computations have been carried out on the states \( \psi_3^s \) and \( \psi_1^t \). Using the SCF orbitals of \( \psi_3^s \) as the initial orbitals in our model for the SCF on \( \psi_1^t \) and computing the quantities \( A \) and \( B \), we obtain the values 2.082339 and -1.025313 au, respectively. These values correspond to the rotational angle of \( \theta = -11.140^\circ \) needed to mix the initial orbitals in order to obtain the SCF orbitals of \( \psi_3^s \). The singlet energy lowering at this angle is, of course, maximal and amounts to \( \Delta E_1^s = -11.43 \) eV. As a consequence, the singlet wavefunction \( \psi_1^s \) acquires 7.2\% \( \psi_3^s \) character constrained by the equal-weight appearance of \( \psi_3^s \) (see eq. (5)). In other words, the 2s orbital of \( \psi_3^s \) acquires a 3.7\% contribution of the 1s orbital of \( \psi_3^s \) at the SCF level causing a contraction of the former orbital. The 1s orbital obtains, in turn, an equal amount of 2s character, and is thus no longer free of nodes.

Fig. 1 shows the charge-density distribution of the 1s orbital of silicon computed for the (1s2s) triplet and singlet SCF states of \( \text{Si}^{12+} \) (panels (B) and (C),

Fig. 1. Contour diagrams of the charge density distribution of the 1s core orbital in the (A) (singlet) ground state of \( \text{Si}^{10+} \); (B) first triplet state of \( \text{Si}^{12+} \); (C) corresponding (1s2s) singlet state of \( \text{Si}^{12+} \). In all panels, the contour lines correspond to 4, 3, 2, 1, 0.5, 0.1, 0.05 and 0.01 au (from inside to outside). In panel (C), three additional contour circles are plotted: the node (bold circle) embedded in two circles each corresponding to a value of 0.01 au.
respectively). We compare these distributions to that of the 1s orbital of the Si^{10+} ion (panel (A)) reflecting the size of a doubly occupied 1s orbital in the presence of an also doubly occupied 2s orbital. As is immediately seen from fig. 1, the 1s orbital of \( \psi_0 \) reveals a node line (see the bold circle in panel (C)) and considerably increases in volume compared to the 1s orbital of \( \psi_T \) and of Si^{+} (the outermost contour line corresponds to the same value in all parts of fig. 1). This orbital dilatation occurring in \( \psi_0 \) is also clearly visualized in fig. 2 where we have plotted the radial density \( r^2 R_{10}^2 (r) \) of the 1s orbital \( \psi_0 \) and \( \psi_T \) as a function of the distance \( r \) from the nucleus (see the maximum of the broken line at \( r = 0.47 \) au). The node of the 1s orbital of \( \psi_0 \) is computed to appear at \( r = 0.34 \) au. The 1s orbital of \( \psi_T \) (solid curve in fig. 2), by contrast, resembles the typical behavior of a 1s orbital in the absence of any mixing. All the findings substantiate the ability of the analytical model applied entirely to reflect the coupling system of two electrons using only a two-orbital basis (the effect of the virtual orbitals on the transformation from the initial orbitals to the final SCF ones can be neglected to a very good approximation, since they are well separated from the core orbitals). We note that the extent of orbital mixing does not scale with the nuclear charge. This is confirmed by SCF calculations on the corresponding states of helium \(^8\).

We are now in the position to discuss the S–T splittings. We have computed the S–T separations in Si^{12+} and SiX^{2+} (X = H, F) at the SCF level and relate the results to the exact S–T gap for Si^{12+} and approximate values for SiX^{2+} (X = H, F), the latter resulting from Green function calculations (due to the high number of electrons, full configuration-interaction (FCI) calculations are not practicable for SiX^{2+}). At the level of our model, the S–T splitting is given by \( d = 2K_{1s, 2s} \). It is illuminating to study the separations computed using different sets of orbitals obtained from different SCF calculations (for technical details we refer to the appendix and ref. \(^9\)).

Our results are collected in table 1. We incidentally recognize that the S–T separations, \( d = 2K_{1s, 2s} \), are quite close to the “exact” values when computed with the orbitals of \( \psi_T \) and, in particular, of \( \psi_0 \). Calculating, on the other hand, the energies of the singlet states (\( \psi_0 \)), as is more usually done, in their “own” molecular orbital basis, we obtain wrong total energies and, consequently, bad S–T splittings. These results clearly exhibit the dependence of the size of the S–T separation on the choice of the orbital basis.

\(^8\) The basis set used (see ref. \(^14\)) consists of 4s Cartesian Gaussians augmented by a p-type polarization function.

![Fig. 2. Radial densities \( r^2 R_{10}^2 (r) \) of the 1s core orbital of the first triplet state (solid line) and the corresponding (1s2s) singlet state (dashed curve) of Si^{12+} as a function of the distance \( r \) from the nucleus. The node of the 1s orbital in the singlet state (at \( r = 0.34 \) au) and the dilatation of this orbital (compared to that of the triplet state) are clearly seen.](image)
Table 1

Singlet–triplet splittings $\Delta=2K_{12s}$ of the Si(1s2s) double vacancies in Si$X_4$ ($X=H, F$) and two-electron states of Si$^{12+}$, computed with different 1s and 2s orbitals. The “exact” singlet–triplet separations $\Delta$ (exact) are also reported. All energy differences are given in eV.

<table>
<thead>
<tr>
<th>System</th>
<th>$\Delta$</th>
<th>$\Delta$</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ground state $^b$</td>
<td>Si(1s2s) triplet state</td>
<td>Si(1s2s) singlet state</td>
</tr>
<tr>
<td>double-vacancy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiH$_4^+$</td>
<td>10.37</td>
<td>11.96</td>
<td>1.69</td>
</tr>
<tr>
<td>SiF$_4^+$</td>
<td>10.39</td>
<td>12.01</td>
<td>1.68</td>
</tr>
<tr>
<td>two-electron</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si$^{12+}$</td>
<td>13.34</td>
<td>14.74</td>
<td>1.99</td>
</tr>
</tbody>
</table>

$^a$ In the case of SiX$^{12+}$ ($X=H, F$), the “ground” state is characterized by the configuration Si(2s$^{-2}$) where two electrons are removed out of the 2s orbital. The ground state of the Si$^{12+}$ ion is the state with the two electrons occupying the 1s orbital.

$^b$ Value was extracted from Green function computations. For details see ref. [9].

The behavior of the various SCF and exact results on the (1s2s) states of Si$^{12+}$ compare favorably with those obtained for the corresponding dicationic states of SiH$_4$ and SiF$_4$, unambiguously revealing the close relationship between the coupling mechanism of two electrons and two vacancies. This is further evidenced by the fact that the SCF condition (3) analytically derived for a two-electron system has been shown to be also fulfilled (within the accuracy of the calculations) in the double-vacancy systems SiX$_4^{12+}$ ($X=H, F$).

To discuss the numerical findings, we first consider the relevant interactions between the pairs of singlet configurations $\Psi^S/\Psi^S$ and $\Psi^T/\Psi^S$.

$$H_{10} = \langle \Psi^S | \hat{H} | \Psi^S \rangle = \sqrt{2} (h_{2s,1s} + V_{2s,1s,1s,1s}) . \quad (6a)$$
$$H_{12} = \langle \Psi^T | \hat{H} | \Psi^S \rangle = \sqrt{2} (h_{2s,1s} + V_{2s,1s,2s,2s}) . \quad (6b)$$

Using the SCF orbitals of the (1s2s) singlet state $\Psi^S$ of Si$^{12+}$, SiH$_4^{12+}$ and SiF$_4^{12+}$, we compute the coupling $|H_{10}|$ to reach the enormous size of 533.18, 452.28 and 448.12 eV, respectively (for these orbitals $H_{10}$ equals $H_{12}$). As may be anticipated, this large coupling between $\Psi^T$ and $\Psi^S$ is dominated by the off-diagonal element $|h_{2s,1s}|$, which amounts to 379.03, 321.63 and 318.54 eV in Si$^{12+}$, SiH$_4^{12+}$ and SiF$_4^{12+}$, respectively, and is a result of the strong 1s/2s orbital mixing in $\Psi^T$. Using, on the other hand, the SCF orbitals of the $\Psi^T$ state to compute the above couplings, we get a value of 20.79 eV for $H_{10}$ (and $-H_{12}$) in the case of Si$^{12+}$. If we finally calculate the coupling $H_{10}$ for Si$^{12+}$ with the SCF orbitals of $\Psi^S$, one finds $H_{10}=0$ according to Brillouin’s theorem. Now the results of table 1 become readily clear. In the SCF calculations on $\Psi^T$, the enormous coupling to $\Psi^S$ (and $\Psi^S$) is obviously neglected leading to a considerable energy lowering of $\Psi^T$, and thus to much too small S–T separations. We notice that in spite of the large energy gap between the 1s and 2s orbitals of $\Psi^S$ (1757.88, 1662.65 and 1665.92 eV in Si$^{12+}$, SiH$_4^{12+}$ and SiF$_4^{12+}$, respectively), the configuration interaction increases the S–T splitting by about an order of magnitude.

From the results of table 1, we know that the S–T separations are reasonably reproduced when using the orbitals of $\Psi^T$ or $\Psi^S$ for their computation. This finding is in line with the small and even vanishing coupling $H_{10}$ (see the data on Si$^{12+}$) resulting when using these orbitals. The quality of the S–T splittings depends on the appearance and strength of $|H_{10}|$, which, in turn, is a function of the orbitals chosen. The large size of $|H_{10}|$ and $|H_{12}|$ found in the $\Psi^S$ orbital basis is a clear artifact of the SCF procedure, which can be remedied up to an essential part only by allowing the interaction between the three configurations $\Psi^S$, $\Psi^S$ and $\Psi^S$. In fact, due to the small influence of valence configurations, we find that such a three-configuration CI is already sufficient to recover an energy of $\Psi^T$ which is only 0.62 eV above the FCI value, i.e. we obtain an energy increase of 12.60 eV (!) from the SCF result. By further allow-
ing for self-consistent orbital optimization within this restricted CI space (multiconfiguration (MC) SCF), we find that the final singlet energy deviates only by 0.14 eV from that obtained by FCI and the resulting S–T separation of 14.14 eV lies very close to the exact value (see table 1). By conceptually replacing electrons by holes, one sees clearly that similar results would be obtained for the S–T separation in the SiX_{1}^{+} (X=H, F) core-hole systems.

Obviously, a complete MCSCF procedure is an appropriate tool to solve the S–T separation problem. However, it seems also possible to introduce “appropriate” orbitals which reproduce the S–T separation quite well already at the one-particle level. The question arises whether the SCF orbitals of the triplet state have something special because they approximate the exact solutions reasonably well. Using the Roothaan canonicalization \[15\] as done in the SCF calculations means that the SCF orbitals of \(\psi^{T}\) satisfy the following condition:

\[\sqrt{2} \tilde{H} - 2h_{2s,1s} + V_{2s,1s,1s,1s} + V_{1s,2s,2s,2s} = 0.\]  

\(7\)

As is immediately extracted from eq. (6), the quantity \(\tilde{H}\) is just the “average” coupling between the configuration \(\psi_{1}^{1}\) and \(\psi_{1}^{0}, \psi_{2}^{0}\), i.e. \(\tilde{H} = \frac{1}{2}(H_{10} + H_{12})\). The Roothaan canonicalized SCF triplet orbitals compel \(\tilde{H}\) to vanish and thus yield a reasonable description of \(\psi_{1}^{1}\). To understand this more closely, we consider the configuration-interaction problem among \(\psi_{2}^{1}, \psi_{2}^{0}\) and \(\psi_{2}^{0}\) (corresponding to the full CI in the two-orbital model). We note that it is not possible to make both the couplings \(H_{10}\) and \(H_{12}\) vanish simultaneously. To determine the best set of orbitals thus means to find those orbitals which maximize the CI coefficient of \(\psi_{1}^{1}\) as a function of the rotational angle \(\theta\). This allows us to approximate \(\psi_{1}^{1}\) as far as possible by a single determinant. Since this leads to lengthy expressions, we approximately solve the problem by making use of perturbation theory and maximize the weight of \(\psi_{1}^{1}\) in second order which is equivalent to minimizing

\[\frac{\tilde{H}_{10}}{|E_{1}^{1} - E_{0}^{1}|^2} + \frac{\tilde{H}_{12}}{|E_{1}^{2} - E_{2}^{2}|^2},\]  

\(8\)

with respect to the orbital mixing angle \(\theta\) (the tilde on \(\tilde{H}_{ij}\) (\(i, j=0, 1, 2\)) and \(E_{i}\) indicates that they are expressed in terms of general orbitals 1s and 2s obtained by rotating the SCF orbitals 1s and 2s of the triplet state). Since both energy denominators are very large, similar in magnitude and vary only slightly with \(\theta\), we may set them equal and independent of \(\theta\). As the result of the minimization we obtain

\[\sin 4\theta \left(1 - \frac{4B^2 - A^2}{D^2} \cos 4\theta + \frac{4AB}{D^2} \sin 4\theta \right) = \frac{2AB}{D^2},\]  

\(9a\)

where

\[D = h_{1s,1s} - h_{2s,2s} + \frac{1}{2}(V_{1s,1s,1s,1s} - V_{2s,2s,2s,2s}).\]  

\(9b\)

\(\theta\) can be estimated by

\[\sin 4\theta \approx 2AB/D^2,\]  

\(9c\)

since \(D^2\) is large compared to \(4AB\). For example, for Si^{12+} the quantities \(A, B\) and \(D\) have been computed to amount to 2.03386, 1.08048 and -70.29261 au (1), respectively. Solving eq. (9a) iteratively, we obtain a rotational angle \(\theta = 0.013^\circ\) which is nearly zero. Consequently, the optimal orbitals are close to the SCF orbitals of the triplet state when using the common Roothaan canonicalization. These orbitals allow us to approximate the exact singlet state quite accurately by a single determinant and, as a consequence, to determine good S–T splittings at the one-particle level.

3. Summary and conclusions

In the present work we have analyzed the problem of singlet–triplet separation found for the Si(1s2s) double vacancies of silane and tetrafluorosilane at the SCF level. By means of a two-electron two-orbital model and numerical applications to SiX_{1}^{+} (X=H, F) and the related two-electron system Si^{12+}, we could identify a considerable mixing of the 1s and 2s core orbitals of silicon to be responsible for the artificial energy lowering observed for the Si(1s2s) singlet states. This mixing has been shown to be a deficiency inherent to the SCF procedure itself that, driven by the variational principle, tries to mimic the next lower-lying (closed-shell) singlet state by decreasing the 2s orbital in volume. The resulting enormous coupling between the 1s and 2s orbitals in the singlet states induces an effective configuration
interaction. The neglect of this interaction by SCF causes the unphysical singlet energy lowering, which is as large as 10 eV for silicon. The corresponding triplet states are not affected by the above deficiencies and we assume them to be reliably predicted by the SCF procedure (this has been supported by the FCI computation performed on $\psi^T$ of Si$^{12+}$). Consequently, the SCF procedure results in grossly incorrect singlet–triplet separation values.

The key point emerging from our analysis, and which is worth restressing, is that a strong configuration interaction appears in the singlet state although the 1s/2s orbital energy separations are of considerable size. Usually, the configuration-interaction coupling elements are not expected to be large for valence states as has been found in, for instance, the Auger spectra of a series of hydrocarbons [12,13]. In the case of core orbitals, however, we find that, if orbital mixing occurs, enormous coupling elements appear because these orbitals are strongly localized in space.

We have shown in the present work that, with an appropriate choice of orbitals, it is still possible to obtain good estimates of the S–T splittings at the one-particle level. In particular, we have proven the interesting result that Roothaan canonicalized triplet orbitals force the average coupling between singlet configurations to vanish, thus yielding approximately correct first-order singlet energies.

The present study confirms that SCF results on multiple vacancy (unpaired electron) systems should generally be considered with care. SCF on excited states of any given symmetry is by principle not guaranteed to give the right answer and it will always run the risk of variational collapse. Even the constraint of a different occupation pattern in the higher state may not hinder the collapse because of orbital mixing. This collapse is obviously incomplete, and in many situations the constraint is sufficient for obtaining reliable results. We have shown here that for core electrons, the magnitude of the constrained collapse is enormous. Clearly, a MCSCF approach incorporating all relevant configurations will handle the problem correctly. In some cases, however, it is not a priori evident which are the configurations of relevance and, in addition, their number might be large. For double-core-vacancy states, even a MCSCF may collapse to the lower-lying valence-vacancy states. It is, hence, also of practical relevance to know that using other sets of orbitals may help to solve the problem as illustrated in this work.

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Appendix. Computational details

The self-consistent-field Hartree–Fock (SCF) calculations on Si$^{12+}$ have been performed using a 12s/9p Cartesian Gaussian basis set contracted to 6s/5p [16]. The SCF computations on silane and tetrafluorosilane with double vacancies in the core of the Si atom have been carried out as described elsewhere [9]. To compute the total energies of Si$^{12+}$, we have also carried out full configuration-interaction (FCI) calculations on the electronic ground state ($1s^2$) and on the first excited ($1s2s$) singlet and triplet states. On the double-core vacancies in SiX$_4$ ($X=\text{H, F}$), we have applied, in addition to the SCF procedure, a Green function method allowing for the computations of the binding energies of double-core holes correct to second order of perturbation theory. The particular scheme used here and in previous works [6,7,9,11–13] is referred to as ADC (algebraic diagrammatic construction). The description of the Green function ADC(2) calculations are given in ref. [9]. The experimental equilibrium nuclear geometries of the neutral molecules in the electronic ground state have been used in the computations on the SiX$_4^+$ ($X=\text{H, F}$) systems [17].

The SCF computations on double-vacancy systems have shown [9] that it is variationally difficult for the SCF method to access higher-lying double-hole states in the presence of lower-lying dicaticionic states of the same symmetry. Obviously, SCF calculations on double-hole states involve more difficulties than those on single-hole states as the problem of variational collapse is much more severe in the case of two vacancies, in particular, when they are located in the core. To satisfy the symmetry condition for the state in question the orbitals are entirely allowed to mix with each other during the SCF optimization. Lack-
ing some computational device to prevent this mixing, the SCF procedure variationally collapses to lower-lying states of appropriate symmetry. One obvious possibility to avoid the variational collapse and to force convergence of the SCF procedure on the desired excited double-vacancy state is to perform a MCSCF calculation with an “active” configuration space including all energetically lower-lying configurations of appropriate symmetry. This is, of course, of little practical relevance for systems of the size of SiX₄ (X = H, F).

In the present cases, we have proceeded as follows: By some computational device [6,7,18] and the use of “appropriate” starting vectors we could improve the convergence properties of the SCF procedure. To determine the appropriate starting vectors, we have carried out SCF calculations on the valence dicative ground and excited states of SiX₄ (X = H, F). These orbitals have then served as starting vectors for the double-core-vacancy states. In particularly delicate cases, we may advance in steps. The orbitals obtained can be used to derive converged SCF computations for successively higher-lying states until the double-core-vacancy states are reached. Details will be given elsewhere [18].

References