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# Double vacancies in the cores of silane and tetrafluorosilane

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The double core vacancies in silane and tetrafluorosilane are theoretically investigated. The corresponding wave functions and energies are computed using propagator methods, and the results are analyzed in some detail. The analysis is performed by breaking up their binding energies into the most relevant components, such as the hole-hole interaction terms and many-body contributions. An unexpectedly large number of satellite states are predicted, which we take as a possible indication that a breakdown of the molecular-orbital picture of double ionization could also occur in *core*-vacancy situations. By comparing with self-consistent-field (SCF) results, we encounter an interesting singlet-triplet separation problem that should be typical for multiple vacancies and is shown to be attributed to a deficiency inherent to the SCF procedure itself. The results on the double core holes in Si$X_4$ ($X$ =H,F) are compared and related to single core vacancies and to experimental data on corresponding double-core-excited states.

## I. INTRODUCTION

The removal of a single core electron in atoms, molecules, and solids has been investigated in many experimental and theoretical studies and is still a popular topic.[1] In contrast to the creation of single core vacancies, much less attention has been paid to the creation of a double or multiple vacancy in the core. Technical reasons and the smaller cross sections make the creation of doubly core-ionized states and their experimental detection difficult. We mention that the cross section is enhanced when considering heavy atoms. To the knowledge of the authors, no experimental results are yet available for molecular double-core-vacancy states. A few theoretical investigations on these states have been carried out.[2,3] On the other hand, experiments on double vacancies in the core of argon[4] and of heavier atoms (e.g., nickel[5] and copper[6]) give rise to the hope that for molecules double-core-hole states can also be expected to be produced and analyzed in the near future. This assumption is supported by the recently reported finding that double-core-vacancy-excited states of molecules have been observed in gas-phase photoabsorption spectra.[7,8] In these experiments two core electrons are excited simultaneously by absorption of a single photon of sufficiently high energy. The energies of the double-core-vacancy-excited states converge to the double-ionization potentials and, therefore, these experiments allow for an estimate of the binding energies of the corresponding double-core-hole states, e.g., the energies needed to *eject* two electrons out of the core.

In the present paper, we are interested in the binding energies of double core vacancies in molecular systems. We focus on the double-core-hole states in silane ($SiH_4$) and tetrafluorosilane ($SiF_4$). Lacking experimental results on double-core-hole states of these molecules we compare our theoretical results with the experimental data available for the corresponding double-core-vacancy–excited states.[7] Both silicon compounds have a central atom with more than a single core orbital and thus a manifold of doubly core-ionized states can be created where both vacancies are localized on the same atom. The detachment of the core electrons can take place either out of the same or out of different spatial orbitals. In the latter case the spins of the remaining electrons can be coupled to singlet or triplet double-core-hole states. For tetrafluorosilane the number of possible double-core-vacancy states is further increased by the fluorine atoms. The existence of the fluorine core orbitals allows for another type of double-core-hole state where the holes are created at different atoms. We refer to these states as *two-center* double-core-vacancy states. In analogy, the other states are called *single-center* states. The binding energies of these different types of doubly core-ionized states of silane and tetrafluorosilane are calculated and analyzed. Particular attention is paid to the response of the systems to the sudden creation of a double vacancy in the cores. For that purpose we study the relaxation processes as well as the repulsion effects occurring in the double-core-hole states. By comparing single and double core ionization energies we try to reveal the relation among these vacancies for the general class of molecules consisting of at least one atom with more than a single core orbital.

## II. TECHNICAL DETAILS OF THE COMPUTATIONS

For the investigation of the double-core-hole states of silane and tetrafluorosilane we have applied two different types of methods. Within one of these approaches

Green's functions are used allowing for the direct computations of the desired binding energies of double core holes. These are the energies needed to eject two electrons out of the core from a system and they are given as negative poles of the particle-particle ($p$-$p$) propagator[9,10] in energy space. The $p$-$p$ propagator has already been applied to compute doubly ionized valence states.[11–15] Numerical results on double-core-hole states of hydrocarbons computed by this method are also available.[2] The particular scheme used here and in previous works[12–15] to approximate the $p$-$p$ propagator is referred to as algebraic diagrammatic construction (ADC). The ADC($n$) scheme consists of all terms up to and including $n$th order of the perturbation expansion of the propagator and approximates higher orders by infinite partial summation of terms. For the $p$-$p$ propagator the scheme is derived and discussed up to second ($n=2$) and third ($n=3$) order in Refs. 16 and 17, respectively. The general computational details are given in Refs. 12(a) and 13(b).

In the present paper, we have applied the second-order ADC scheme ($n=2$) to the $p$-$p$ propagator so that the ADC space is spanned by all dicationic configurations, which can be classified as two-hole ($2h$) and three-hole–one-particle ($3h$-$1p$) configurations with respect to the neutral ground state. Being interested in states with two vacancies in the *core*, the so-called core-valence separation has been used in this work (the number of core vacancies is preserved in all configurations). To assess the inaccuracy introduced by this approximation we have also carried out for $SiH_4$ full-configuration-space calculations without imposing the core-valence separability. In the large $SiF_4$ molecule the highest five virtual orbitals that are energetically well separated from the other virtual ones have been excluded from the active configuration space. The impact of this restriction of the active space on the final results has been found computationally to be quite small: the ADC eigenvalues, i.e., the binding energies of the double core vacancies, are subject to an average shift of 0.42 eV to lower energy.

The orbital energies and Coulomb integrals resulting from self-consistent-field Hartree-Fock (SCF-HF) computations on the neutral ground state serve as input data for the Green's-function ADC(2) calculations performed in this work on the $SiH_4$ and $SiF_4$ molecules. For both molecules we have used in the SCF-HF calculations a double-zeta plus polarization (DZP) basis set consisting of $6s,4p,$[18]$1d$ Cartesian Gaussians on silicon; $2s,1p$ on each hydrogen;[19] and $4s,2p,$[19]$1d$ on each fluorine. The exponential scaling factor for the $s$ and $p$ functions on hydrogen are 1.2 and 1.0, respectively. The exponent for the $d$ functions on silicon is chosen as 0.39 for both molecules.[20] The exponent for the $d$ functions on fluorine is taken to be 1.62.[20] The total number of basis functions thus amounts to 44 and 88 for $SiH_4$ and $SiF_4$, respectively. The experimental equilibrium geometries of the neutral ground-state molecules have been utilized.[21] The silicon-hydrogen distance is 1.4798 Å and the silicon-fluorine distance 1.55 Å. The resulting ground-state HF total energies are (in a.u.) $-291.247\,681$ and $-687.061\,541$ for $SiH_4$ and $SiF_4$, respectively.

For $SiH_4$, the full configuration spaces have the dimensions 2115 ($^1A$), 2832 ($^3A$), 2110 ($^1B_i$, $i=1-3$), and 2848 ($^3B_i$, $i=1-3$), when using the Abelian subgroup $D_2$ and the basis set specified above. Without imposing the separability of core and valence electrons we obtain in the case of $SiF_4$ spaces spanned by as many as 75 491 ($^1A$), 108 798 ($^3A$), 75 478 ($^1B_i$, $i=1-3$), and 108 834 configurations ($^3B_i$, $i=1-3$). In the restricted configuration spaces generated by imposing the core-valence separation, the dimensions of the ADC(2) eigenvalue problems decrease to 1231 ($^1A$), 1659 ($^3A$), 1228 ($^1B_i$, $i=1-3$), and 1667 ($^3B_i$, $i=1-3$) for $SiH_4$. In the case of $SiF_4$, we are still left with 22 287 ($^1A$), 31 842 ($^3A$), 22 282 ($^1B_i$, $i=1-3$), and 31 854 configurations ($^3B_i$, $i=1-3$). These dimensions result if we count the $1s$, $2s$, and $2p$ electrons of Si and the $1s$ electrons of F as core electrons.

In addition to the ADC(2) computations we have also carried out so-called ΔSCF calculations in order to determine binding energies of double-core-hole states in silane and tetrafluorosilane at the SCF level. These computations are based upon separate SCF calculations for the system's ground state and the dicationic state under consideration. The basis sets and geometries used in the ΔSCF calculations are the same as specified above.

### III. NUMERICAL RESULTS ON THE DOUBLY IONIZED CORES

Both the silicon molecules, silane ($SiH_4$) and tetrafluorosilane ($SiF_4$), have a tetrahedral structure and belong to the symmetry group $T_d$. The electronic ground state of neutral silane and tetrafluorosilane are closed-shell singlet states of $A_1$ symmetry and are described by the following configurations:

$SiH_4$

| | | | |
|---|---|---|---|
| Core orbitals | $1a_1^2$ | $2a_1^2$ | $1t_2^6$ |
| | Si(1$s$) | Si(2$s$) | Si(2$p$) |
| Valence orbitals | $3a_1^2 2t_2^6$ | | |
| | Si—H bond | | |

$SiF_4$

| | | | | |
|---|---|---|---|---|
| Core orbitals | $1a_1^2$ | $1t_2^6 2a_1^2$ | $3a_1^2$ | $2t_2^6$ |
| | Si(1$s$) | F(1$s$) | Si(2$s$) | Si(2$p$) |
| Valence orbitals | $4a_1^2 3t_2^6$ | | $5a_1^2 4t_2^6 1e^4 5t_2^6 1t_1^6$ | |
| | Si—F bond | | F lone pairs and Si—F bond | |
| | Inner valence | | Outer valence | |

The orbitals are divided into a core and a valence part. The specifications of the orbitals are also reported. We wish to point out that the core orbital spaces defined here are spanned by three and five orbitals for $SiH_4$ and $SiF_4$, respectively. The core-valence separation we have applied in the ADC(2) computations on these molecules is based upon the appealing argument that, for core and valence electrons, the differences in the localization in space and in energy are quite large. In Table I we present the HF orbital energies $\varepsilon$ of silane and tetrafluorosilane. Considering only the Si(1*s*) orbital as a pure core orbital, the energy gap between the core and valence orbitals amounts to 1851.5 and 1831.0 eV in silane and tetrafluorosilane, respectively. The gap is reduced in silane to a value of 95.1 eV and in tetrafluorosilane of 74.3 eV when including the 2*s* and 2*p* orbitals of silicon in the core space as well. For $SiF_4$, the extended core space additionally comprises the 1*s* orbitals of the four fluorine atoms. Because of the localized nature of the four equivalent fluorine atoms, the $1t_2$ and $1a_1$ orbitals (originating from the same type of parent orbital) are nearly degenerate.

Up to now there is, to our knowledge, no experience available on the core-valence separation in the case of two core vacancies. Imposing the separability of the core and valence electrons means that the ADC space is limited to include only those dicationic configurations that have two holes in the core orbital space independent of the number of excitations of the valence electrons.[3] The impact of this approximation on the binding energies and manifold of the double-core-hole states will be discussed in some detail in Sec. IV.

The 10 core electrons in silane are distributed over 3 orbitals and allow for the creation of 12 (8 singlets and 4 triplets) double-core-hole states: 5 states of $A_1$ symmetry (4 singlets and 1 triplet), 1 singlet state of $E$ symmetry, 1 triplet state of $T_1$ symmetry, and 5 states of $T_2$ symmetry (3 singlets and 2 triplets). Because of the high number of 18 core electrons in tetrafluorosilane (distributed over 5 orbitals) already 37 double-core-hole states can be created when annihilating 2 core electrons from the neutral ground-state electronic configuration: 13 states of $A_1$ symmetry (9 singlets and 4 triplets), 4 states of $E$ symmetry (3 singlets and 1 triplet), 4 states of $T_1$ symmetry (1 singlet and 3 triplets), and 16 states of $T_2$ symmetry (9 singlets and 7 triplets). In total 22 singlet and 15 triplet states result.

In Table II we have reported the binding energies and character of the Si single-center double-core-vacancy states for silane and tetrafluorosilane with at least one vacancy in the 1*s* orbital. All the states and energies are computed via ADC(2). In the framework of our approach, the character of a state is defined by the associated leading configurations and the squares of the corresponding components of the ADC eigenvectors. As already anticipated from the HF orbital energies (see Table I, in particular, the quantity $2\varepsilon$), the energies needed to eject the two 1*s* electrons is enormous for both molecules. Interestingly, the substitution of hydrogen by fluorine shifts the 1*s* double binding energy by 12.58 eV. The ex-

TABLE I. Energies of the occupied HF molecular orbitals in the electronic ground-state configurations of silane and tetrafluorosilane, computed at the experimentally determined equilibrium geometries (Ref. 21).

| No.[a] | Orbital | Symmetry | $\varepsilon$ (a.u.) | $-2\varepsilon$ (eV) |
|---|---|---|---|---|
| | | $SiH_4$ core | | |
| 1 | Si(1*s*) | $1a_1$ | −68.772 822 | 3742.8454 |
| 2 | Si(2*s*) | $2a_1$ | −6.122 637 | 333.2142 |
| 3 | Si(2*p*) | $1t_2$ | −4.229 289 | 230.0860 |
| | | $SiH_4$ valence | | |
| 4 | | $3a_1$ | −0.732 052 | 39.8408 |
| 5 | | $2t_2$ | −0.485 934 | 26.4462 |
| | | $SiF_4$ core | | |
| 1 | Si(1*s*) | $1a_1$ | −68.967 418 | 3753.4358 |
| 2 | F(1*s*) | $1t_2$ | −26.337 996 | 1433.4012 |
| 3 | F(1*s*) | $2a_1$ | −26.337 975 | 1433.4000 |
| 4 | Si(2*s*) | $3a_1$ | −6.300 849 | 342.9132 |
| 5 | Si(2*p*) | $2t_2$ | −4.410 322 | 240.0244 |
| | | $SiF_4$ valence | | |
| 6 | | $4a_1$ | −1.681 616 | 91.5192 |
| 7 | | $3t_2$ | −1.642 623 | 89.3970 |
| 8 | | $5a_1$ | −0.868 440 | 47.2634 |
| 9 | | $4t_2$ | −0.789 420 | 42.9628 |
| 10 | | $1e$ | −0.735 477 | 40.0270 |
| 11 | | $5t_2$ | −0.714 965 | 38.9108 |
| 12 | | $1t_1$ | −0.680 575 | 37.0392 |

[a] The orbitals are numbered going from the core to the valence region.

TABLE II. Binding energies and character (leading configurations with the squares of the corresponding components of the ADC eigenvectors) of single-center double-core-vacancy states in silane and tetrafluorosilane computed by ADC(2), imposing the separability of core and valence electrons. For details see the text. The $2h$ components are underlined. All the $3h$-$1p$ components larger than or equal to 0.01 are reported.

| | | | Silane | | Tetrafluorosilane | |
|---|---|---|---|---|---|---|
| No. | Specification[a] | State | Energy (eV) | Character | Energy (eV) | Character |
| 1 | $\mathrm{Si}(1s^{-2})$ | $^1A_1$ | 3919.86 | $\underline{0.75}\ 1a_1^{-2}$<br>$0.08\ 1a_1^{-2}2t_2^{-1}4t_2^{+1}$<br>$0.03\ 1a_1^{-2}3a_1^{-1}4a_1^{+1}$<br>$0.02\ 1a_1^{-2}3a_1^{-1}9a_1^{+1}$<br>$0.01\ 1a_1^{-2}2a_1^{-1}13a_1^{+1}$ | 3932.44 | $\underline{0.77}\ 1a_1^{-2}$<br>$0.03\ 1a_1^{-2}4t_2^{-1}7t_2^{+1}$<br>$0.03\ 1a_1^{-2}5a_1^{-1}7a_1^{+1}$ |
| 2 | $\mathrm{Si}(1s^{-1}2s^{-1})$ | $^1A_1$ | 2070.16[b] | $\underline{0.73}\ 1a_1^{-1}2a_1^{-1}$<br>$0.13\ 1a_1^{-1}2a_1^{-1}2t_2^{-1}4t_2^{+1}$<br>$0.05\ 1a_1^{-1}2a_1^{-1}3a_1^{-1}4a_1^{+1}$<br>$0.02\ 1a_1^{-1}2a_1^{-1}3a_1^{-1}9a_1^{+1}$ | 2082.30[b] | $\underline{0.76}\ 1a_1^{-1}3a_1^{-1}$<br>$0.05\ 1a_1^{-1}3a_1^{-1}4t_2^{-1}7t_2^{+1}$<br>$0.04\ 1a_1^{-1}3a_1^{-1}5a_1^{-1}7a_1^{+1}$<br>$0.01\ 1a_1^{-1}3a_1^{-1}5a_1^{-1}6a_1^{+1}$ |
| 3 | $\mathrm{Si}(1s^{-1}2s^{-1})$ | $^3A_1$ | 2059.39[b] | $\underline{0.73}\ 1a_1^{-1}2a_1^{-2}$<br>$0.12\ 1a_1^{-1}2a_1^{-1}2t_2^{-1}4t_2^{+1}$<br>$0.04\ 1a_1^{-1}2a_1^{-1}3a_1^{-1}4a_1^{+1}$<br>$0.02\ 1a_1^{-1}2a_1^{-1}3a_1^{-1}9a_1^{+1}$ | 2071.71[b] | $\underline{0.76}\ 1a_1^{-1}3a_1^{-1}$<br>$0.05\ 1a_1^{-1}3a_1^{-1}4t_2^{-1}7t_2^{+1}$<br>$0.04\ 1a_1^{-1}3a_1^{-1}5a_1^{-1}7a_1^{+1}$<br>$0.01\ 1a_1^{-1}3a_1^{-1}5a_1^{-1}6a_1^{+1}$ |
| 4 | $\mathrm{Si}(1s^{-1}2p^{-1})$ | $^1T_2$ | 2018.55 | $\underline{0.73}\ 1a_1^{-1}1t_2^{-1}$<br>$0.12\ 1a_1^{-1}1t_2^{-1}2t_2^{-1}4t_2^{+1}$<br>$0.04\ 1a_1^{-1}1t_2^{-1}3a_1^{-1}4a_1^{+}$<br>$0.02\ 1a_1^{-1}1t_2^{-1}3a_1^{-1}9a_1^{+1}$ | 2031.07 | $\underline{0.76}\ 1a_1^{-1}2t_2^{-1}$<br>$0.04\ 1a_1^{-1}2t_2^{-1}4t_2^{-1}7t_2^{+1}$<br>$0.04\ 1a_1^{-1}2t_2^{-1}5a_1^{-1}7a_1^{+1}$<br>$0.01\ 1a_1^{-1}2t_2^{-1}5a_1^{-1}6a_1^{+1}$ |
| 5 | $\mathrm{Si}(1s^{-1}2p^{-1})$ | $^3T_2$ | 2012.34 | $\underline{0.74}\ 1a_1^{-1}1t_2^{-1}$<br>$0.12\ 1a_1^{-1}1t_2^{-1}2t_2^{-1}4t_2^{+1}$<br>$0.04\ 1a_1^{-1}1t_2^{-1}3a_1^{-1}4a_1^{+1}$<br>$0.02\ 1a_1^{-1}1t_2^{-1}3a_1^{-1}9a_1^{+1}$ | 2024.78 | $\underline{0.76}\ 1a_1^{-1}2t_2^{-1}$<br>$0.05\ 1a_1^{-1}2t_2^{-1}4t_2^{-1}7t_2^{+1}$<br>$0.04\ 1a_1^{-1}2t_2^{-1}5a_1^{-1}7a_1^{+1}$<br>$0.01\ 1a_1^{-1}2t_2^{-1}5a_1^{-1}6a_1^{+1}$ |

[a] The specification is given with respect to the parent orbitals of silicon.

[b] Here the $2p$ orbital of silicon was excluded from the core space and attributed to the valence space.

tended core orbital space allows for the removal of two electrons out of *different* core orbitals and, thus, for the study of singlet-triplet splittings in double-core-hole states (see Sec. V B for more details). The binding energies of the remaining Si single-center double-core-hole states in silane and tetrafluorosilane are collected in Table III. The states with one or two holes in the $1s$ core orbital of a fluorine atom are considered separately (see Table IV) and discussed below. For reasons that become clear in Sec. IV, we have excluded the $2p$ orbital of silicon from the core space and attributed it to the "valence" part in some cases [for the singlet-triplet pairs of $A_1$ symmetry in Table II and the $^1A_1$ $\mathrm{Si}(2s^{-2})$ states in Table III].

As expected for double-ionization processes out of core orbitals, the vacancies are strongly localized in the dicationic states of $\mathrm{Si}X_4$ ($X=\mathrm{H,F}$) and a clustering of states with similar hole distribution results (see Tables II and III). The single-center states decompose into three distinct groups and can be characterized according to their hole distribution: above 3900 eV (binding energy) the $\mathrm{Si}(1s^{-2})$-derived states occur; between 2010 and 2085 eV we encounter the $\mathrm{Si}(1s^{-1}2s^{-1})$- and $\mathrm{Si}(1s^{-1}2p^{-1})$-type states; and finally, from 248 to 367 eV, those characterized by the $\mathrm{Si}(2s^{-2})$, $\mathrm{Si}(2s^{-1}2p^{-1})$, and $\mathrm{Si}(2p^{-2})$ popula-

TABLE III. Binding energies of energetically lower lying single-center doubly ionized core states in silane and tetrafluorosilane computed by ADC(2), assuming the separability of core and valence electrons. For details see the text.

| | | | Energy (eV) | |
|---|---|---|---|---|
| No. | Specification[a] | State | Silane | Tetrafluorosilane |
| 1 | $\mathrm{Si}(2s^{-2})$ | $^1A_1$ | 354.90[b] | 366.56[b] |
| 2 | $\mathrm{Si}(2s^{-1}2p^{-1})$ | $^1T_2$ | 313.86 | 333–330[c] |
| 3 | $\mathrm{Si}(2s^{-1}2p^{-1})$ | $^3T_2$ | 296.08 | 312–309[c] |
| 4 | $\mathrm{Si}(2p^{-2})$ | $^1A_1$ | 259.21 | 271.03 |
| 5 | $\mathrm{Si}(2p^{-2})$ | $^1E$ | 253.80 | 265.62 |
| 6 | $\mathrm{Si}(2p^{-2})$ | $^1T_2$ | 253.80 | 265.62 |
| 7 | $\mathrm{Si}(2p^{-2})$ | $^3T_1$ | 248.28 | 260.07 |

[a] The specification is given with respect to the parent orbitals of silicon.

[b] Here the $\mathrm{Si}(2p)$ orbital was excluded from the core space and attributed to the valence space.

[c] From a not fully converged ADC(2) calculation, the eigenvalue was estimated to lie in the specified energy region.

tion.

After having presented briefly the numerical results on the single-center double-core-hole states in Si$X_4$ ($X$=H,F), we turn to the two-center double vacancies possible in the core of $SiF_4$. Two types of two-center states can be created in $SiF_4$: states where the vacancies are located on *equivalent* (two fluorine atoms) or *different* atoms (the silicon and one of the fluorine atoms) and thus, we can expect the two-center states to cluster in two groups. Table IV shows the binding energies and character of these states computed via ADC(2). Indeed, we obtain a group at 1403.88 eV, corresponding to states with two holes on distinct fluorine atoms [for these states we have introduced the shorthand notation $F_1(1s^{-1})F_j(1s^{-1})$ with $i \neq j$, see Table IV] and a group comprising states with one hole on a fluorine atom and one on silicon. Within the latter group we observe a further clustering of the states in three subgroups according to their hole distribution (over the core orbitals of Si): at 2569 eV we see the $F(1s^{-1})Si(1s^{-1})$-type states; at 876 eV those characterized by the $F(1s^{-1})Si(2s^{-1})$ configuration; and finally, at 820 eV the $F(1s^{-1})Si(2p^{-1})$-derived states appear. The clustering of states as well as the energy gaps between the groups and subgroups clearly demonstrate the localized nature of core orbitals.

The behavior of the electrostatic repulsion between the two holes allows us to distinguish between single- and two-center double-core-vacancy states. Due to the more efficient hole-hole repulsion, single-center states are expected to appear at higher energies than related two-center states. A look at Table IV reveals another general feature of dicationic two-center states: corresponding singlet-triplet pairs are nearly degenerate. The singlet-triplet splittings are found to be smaller than 0.01 eV. This is in sharp contrast to the case of single-center double-core-hole states where the splitting is very large (see Tables II and III). The near degeneracy of corresponding singlet-triplet pairs of two-center states reflects the short-range exchange interaction between the holes (see also Sec. V A).

## IV. IMPACT OF CORE-VALENCE SEPARATION AND SATELLITE STATES

In the present paper, we have applied the core-valence separation to an *extended* core orbital space. Therefore, it seems natural to pose the question whether it remains a good approximation even if the core orbital space comprises *more* than a single orbital. To answer this question, we have computed the binding energies of the double core vacancies in silane twice, with and without making use of the genuine properties of the core orbitals. For practical reasons we have included in the ADC calculations all the configurations with two and three vacancies in the core when using the core-valence separation. We mention that the latter configurations with more than two holes in the core orbital space need not be taken into account in the strict core-valence separation.[3] The com-

TABLE IV. Binding energies and character (square leading components) of two-center double-core-hole states in tetrafluorosilane computed by ADC(2), imposing the core-valence separation. For details see the text.

| No. | Specification[a] | State | Energy (eV) | Character |
|---|---|---|---|---|
| 1 | $F(1s^{-1})Si(1s^{-1})$ | $^1T_2$ | 2569.16 | 0.78 $1a_1^{-1}1t_2^{-1}$ |
| 2 | $F(1s^{-1})Si(1s^{-1})$ | $^3T_2$ | 2569.17 | 0.78 $1a_1^{-1}1t_2^{-1}$ |
| 3 | $F(1s^{-1})Si(1s^{-1})$ | $^1A_1$ | 2569.16 | 0.78 $1a_1^{-1}2a_1^{-1}$ |
| 4 | $F(1s^{-1})Si(1s^{-1})$ | $^3A_1$ | 2569.17 | 0.78 $1a_1^{-1}2a_1^{-1}$ |
| 5 | $F_i(1s^{-1})F_j(1s^{-1})$[b] | $^1E$ | 1403.88 | 0.74 $1t_2^{-2}$ |
| 6 | $F_i(1s^{-1})F_j(1s^{-1})$[b] | $^1T_2$ | 1403.88 | 0.37 $1t_2^{-2}$, 0.37 $1t_2^{-1}2a_1^{-1}$ |
| 7 | $F_i(1s^{-1})F_j(1s^{-1})$[b] | $^3T_1$ | 1403.88 | 0.74 $1t_2^{-2}$ |
| 8 | $F_i(1s^{-1})F_j(1s^{-1})$[b] | $^3T_2$ | 1403.88 | 0.74 $1t_2^{-1}2a_1^{-1}$ |
| 9 | $F_i(1s^{-1})F_j(1s^{-1})$[b] | $^1A_1$ | 1403.88 | 0.56 $2a_1^{-2}$, 0.19 $1t_2^{-2}$ |
| 10 | $F(1s^{-1})Si(2s^{-1})$ | $^1A_1$ | 872.62[c] | 0.77 $2a_1^{-1}3a_1^{-1}$ |
| 11 | $F(1s^{-1})Si(2s^{-1})$ | $^1T_2$ | 872.62[c] | 0.77 $1t_2^{-1}3a_1^{-1}$ |
| 12 | $F(1s^{-1})Si(2s^{-1})$ | $^3A_1$ | 872.63[c] | 0.77 $2a_1^{-1}3a_1^{-1}$ |
| 13 | $F(1s^{-1})Si(2s^{-1})$ | $^3T_2$ | 872.63[c] | 0.77 $1t_2^{-1}3a_1^{-1}$ |
| 14 | $F(1s^{-1})Si(2p^{-1})$ | $^1A_1$ | 820.72 | 0.77 $1t_2^{-1}2t_2^{-1}$ |
| 15 | $F(1s^{-1})Si(2p^{-1})$ | $^1T_2$ | 820.72 | 0.52 $1t_2^{-1}2t_2^{-1}$, 0.26 $2a_1^{-1}2t_2^{-1}$ |
| 16 | $F(1s^{-1})Si(2p^{-1})$ | $^3A_1$ | 820.74 | 0.77 $1t_2^{-1}2t_2^{-1}$ |
| 17 | $F(1s^{-1})Si(2p^{-1})$ | $^3T_2$ | 820.74 | 0.52 $1t_2^{-1}2t_2^{-1}$, 0.26 $2a_1^{-1}2t_2^{-1}$ |
| 18 | $F(1s^{-1})Si(2p^{-1})$ | $^1E$ | 820.57 | 0.77 $1t_2^{-1}2t_2^{-1}$ |
| 19 | $F(1s^{-1})Si(2p^{-1})$ | $^3E$ | 820.57 | 0.77 $1t_2^{-1}2t_2^{-1}$ |
| 20 | $F(1s^{-1})Si(2p^{-1})$ | $^1T_1$ | 820.57 | 0.77 $1t_2^{-1}2t_2^{-1}$ |
| 21 | $F(1s^{-1})Si(2p^{-1})$ | $^3T_1$ | 820.57 | 0.77 $1t_2^{-1}2t_2^{-1}$ |
| 22 | $F(1s^{-1})Si(2p^{-1})$ | $^1T_2$ | 820.56 | 0.52 $2a_1^{-1}2t_2^{-1}$, 0.26 $1t_2^{-1}2t_2^{-1}$ |
| 23 | $F(1s^{-1})Si(2p^{-1})$ | $^3T_2$ | 820.57 | 0.52 $2a_1^{-1}2t_2^{-1}$, 0.26 $1t_2^{-1}2t_2^{-1}$ |

[a] The specification is given with respect to the parent orbitals, involving those of silicon and fluorine.

[b] $i \neq j$, i.e., the vacancies are located on *different* fluorine atoms.

[c] Here the Si(2*p*) orbital was excluded from the core space and attributed to the valence space.

putations on $SiH_4$ show that a shift of at most 0.25 eV (fourth state of Tables II and III) to lower binding energies results when imposing the core-valence separation and separating ten core electrons. On the average, we obtain a deviation of 0.14 eV. The effect on the binding energies relative to each other is smaller and, thus, these relative energies are nearly unaffected. The small shifts in the binding energies above clearly demonstrate the usefulness of assuming the core-valence separability when evaluating double core vacancies, even if the usual $1s$ core space is extended to include the $2s$ and $2p$ orbitals as well. For the sake of comparison we also report the somewhat larger shift of 0.57 eV caused by introducing the core-valence separability for the double ionization out of the core orbital of a carbon atom.[2(a)]

Another aspect has to be considered when imposing the core-valence separation on a core space comprising more than one orbital. The size of the core space chosen affects the manifold of possible dicationic states. To make this effect transparent some general remarks are in order. From molecule core-level photoelectron spectra it is well known that the single-core-hole main peak can be accompanied by a pronounced satellite structure at its high-binding-energy side.[1] Satellite states are mainly characterized by $2h$-$1p$ and higher excited configurations in the case of single ionization. It is clear from general arguments and from our ADC results that the appearance of satellites can be assumed also in the case of double core ionization. These satellites may be addressed, in analogy to the single-core-ionization event, as shake-up satellites. Because of the higher amount of relaxation present in doubly ionized compared to singly ionized systems we may expect for the former even more intense and lower-lying satellite states than in the latter case (see also Sec. V C). Apart from that, a satellite configuration characterized by four ($3h$-$1p$) instead of three ($2h$-$1p$) open shells already by itself gives rise to a higher manifold of satellite states.[15] Additional many-body effects may occur, which are discussed in the following.

In molecular systems with *more* than a single core orbital two different types of shake-up satellites may occur: the double core vacancy may be accompanied by the excitation of a valence or core electron. Configurations corresponding to the former type we abbreviate by $(2h)_c$-$(1h)_v$-$1p$ indicating that two holes are in the core $c$ and one hole in the valence part $v$. The other type of satellites is characterized by configurations with three holes in the core part denoted by $(3h)_c$-$1p$ in the following. Now, the configurations corresponding to such shake-up satellites arising from a specific double core vacancy $(2h)_c$ may, in principle, interact strongly with $2h$ configurations of *other core* orbitals. This would lead to a breakdown of the familiar molecular-orbital picture of double ionization similar to that commonly encountered in the case of ionization of inner-valence electrons.[22,15] The various core orbitals of different energies formally play the same role as outer- and inner-valence orbitals. Our ADC(2) computations indicate the appearance of the breakdown phenomenon also in double- (and probably also in single-) core-vacancy situations. Two specific examples are discussed below. We would like to stress, however, that since core satellite states are not well described in a second-order scheme like ADC(2), our results may only serve as an indication for the existence of the above-mentioned interesting phenomenon.

In some cases we find strong mixing between the $(2h)_c$ and $(2h)_c$-$(1h)_v$-$1p$ configurations leading to an intense spreading of the $(2h)_c$ components over many states accompanied by the appearance of various $(2h)_c$-$(1h)_v$-$1p$ derived satellites above *and* below the binding energy of the $(2h)_c$-derived states. Typical representatives of states exhibiting these many-body effects are the Si$(2s^{-1}2p^{-1})$-type states (see Table III). The Si$(2s^{-1}2p^{-1})$ configuration strongly interacts with the shake-up configurations derived from a single $1h$-$1p$ excitation of a valence $v$ electron into a virtual orbital $\nu$ on top of Si$(2p^{-2})$. The result is a distribution of the Si$(2s^{-1}2p^{-1})$ component over many states comprising a variety of Si$(2p^{-2}v^{-1}\nu^{+1})$-derived shake-up satellites.

The breakdown phenomenon could, in principle, occur by the interactions of $(2h)_c$ and $(3h)_c$-$1p$ configurations. Let us consider, for instance, the $(3h)_c$-$1p$ configurations Si$(2s^{-1}2p^{-2}\nu^{+1})$ arising from a $1h$-$1p$ excitation on the Si$(2s^{-1}2p^{-1})$ configuration. They have been computed to lie in the energy region of the Si$(2s^{-2})$ configuration and to interact with the latter. Due to the incomplete screening of the $3h$-$1p$ configurations by ADC(2) we assume that the ADC(2) scheme tends to overestimate the $3h$-$1p$ contributions to main states, particularly those of $(3h)_c$-$1p$ configurations. Thus, it is beyond a second-order approximation to decide whether $(3h)_c$-$1p$-derived shake-up satellites occur in double-core-level spectra. Note that the latter type of satellites has no analogy in ionized molecules with only one core orbital. Similarly to the finding in Ref. 23 for single core ionization we expect that the satellites accompanying a double core vacancy are appropriately described by the fourth-order ADC scheme.

In the present work we have applied the second-order scheme and, hence, attributed the Si$(2p)$ to the valence orbitals when calculating those binding energies of double core vacancies affected by the coupling between the $(2h)_c$ and $(3h)_c$-$1p$ at the ADC(2) level [see the $(1s^{-1}2s^{-1})$-type states in Tables II and IV and the Si$(2s^{-2})$ double vacancies in Table III]. Fortunately, the binding energies of the corresponding major double-core-hole states were only slightly affected by the choice of the core orbital space. For the Si$(1s^{-1}2s^{-1})$-derived singlet-triplet pair of silane, for example, we have computed binding energies of 2069.47 and 2058.49 eV for the singlet and triplet states, respectively, when separating the core space comprising ten electrons (instead of four core electrons as in Table II). The very large singlet-triplet separation thus changed only by 0.21 eV.

## V. DISCUSSION

### A. Hole-hole repulsion, relaxation, and other contributions

To analyze computational results we break up the binding energy into several relevant components of different physical origin. The binding energy of the double core vacancy ($a^{-1}b^{-1}$) or the double-ionization potential (DIP, or alternatively denoted by $\mathcal{V}^{\mathrm{DIP}}$ in the equations)

$$\mathcal{V}^{\mathrm{DIP}}=E^{2+}(a^{-1}b^{-1})-E^{0} \tag{1}$$

is given as the difference of the exact total energies of the dicationic state and the ground state of the neutral molecule. It is useful to write

$$\begin{aligned}\mathcal{V}^{\mathrm{DIP}}=&-\varepsilon_a-\varepsilon_b+E_{\mathrm{RE}}(a^{-1}b^{-1})\\&-R(a^{-1}b^{-1})+C(a^{-1}b^{-1})\ ,\end{aligned} \tag{2}$$

where $\varepsilon_a,\varepsilon_b$ are the ground-state orbital energies of the two core orbitals $\phi_a,\phi_b$, and the other quantities are defined in the following.

The two vacancies in $\phi_a$ and $\phi_b$ repel each other electrostatically. This repulsion energy is given by the Coulomb integral

$$V_{abab}=\langle\phi_a(1)\phi_b(2)||\mathbf{r}_1-\mathbf{r}_2|^{-1}|\phi_a(1)\phi_b(2)\rangle\ . \tag{3}$$

If the two vacancies are in different orbitals or in a degenerate orbital, exchange contributions arise as well. The explicit expressions for the *repulsion-exchange* energies $E_{\mathrm{RE}}$ are collected in Table V for all possible Si single-center double core vacancies in Si$X_4$ ($X$=H,F). We note that the removal of two electrons out of a threefold degenerate $t_2$ orbital leads to four states of different symmetry and multiplicity. The exchange integral $V_{abba}$ enters the expressions for the exchange energy in different ways. The Coulomb and exchange integrals can be extracted from SCF-HF calculations on the electronic ground state of the neutral molecule.

Removing two electrons from core orbitals creates a new potential for the remaining electrons that can be accounted for in ΔSCF calculations. In such calculations the DIP is obtained by computing the energies $E^{2+}$ and $E^0$ in Eq. (1) separately at their respective SCF level. The relaxation energy $R$ is defined as the change in binding energy (or DIP) due to the appearance of the new potential at the SCF level. It is determined from the difference

$$-R=\mathcal{V}^{\mathrm{DIP}}_{\Delta\mathrm{SCF}}-(-\varepsilon_a-\varepsilon_b+E_{\mathrm{RE}}) \tag{4}$$

between the ΔSCF energy and that obtained at the frozen-orbital (FO) level of approximation. $R$ is always positive and hence decreases the DIP, as can be seen in Eq. (2).

TABLE V. Repulsion-exchange energies $E_{\mathrm{RE}}$ of all possible Si single-center double core vacancies in silane and tetrafluorosilane. For the definition of the integrals see the text.

| 2$h$ configuration | Repulsion-exchange energy | State |
|---|---|---|
| $s^{-2}$ | $V_{aaaa}$ ($a=\nu s,\nu=1,2$) | $^1A_1$ |
| $s^{-1}s^{-1}$ | $V_{abab}-V_{abba}$ ($a=1s,b=2s$) | $^3A_1$ |
|  | $V_{abab}+V_{abba}$ | $^1A_1$ |
| $s^{-1}p^{-1}$ | $V_{abab}-V_{abba}$ ($a=\nu s,\nu=1,2;b=2p$) | $^3T_2$ |
|  | $V_{abab}+V_{abba}$ | $^1T_2$ |
| $p^{-2}$ | $V_{aaaa}+2V_{abba}$ | $^1A_1$ |
|  | ($a,b=2p$, different components) |  |
|  | $V_{aaaa}-V_{abba}$ | $^1E$ |
|  | $V_{abab}+V_{abba}$ | $^1T_2$ |
|  | $V_{abab}-V_{abba}$ | $^3T_1$ |

The difference $C$ between the exact DIP and the one computed via the ΔSCF procedure arises from correlation effects. As can be seen from Eq. (1), $C$ itself is given by the change of correlation energy in the molecule due to the creation of the double vacancy. For core vacancies, the correlation contribution $C$ is generally believed to be substantially less relevant than the relaxation contribution $R$. We have seen in the preceding section that this is not necessarily the case for particular types of double core vacancies. It should be noted that both relaxation and correlation effects are included in the DIP computed using the ADC(2) scheme. Of course, since this is only a second-order scheme and $R$ is a large number, we cannot expect high accuracy.

To get some quantitative idea of the size of many-body contributions to the binding energies of double core vacancies we have computed them approximately from Eq. (2) after replacing the exact DIP by the one computed via ADC(2) ($\mathcal{V}^{\mathrm{DIP}}_{\mathrm{ADC(2)}}$):

$$R-C\simeq-\varepsilon_a-\varepsilon_b+E_{\mathrm{RE}}-\mathcal{V}^{\mathrm{DIP}}_{\mathrm{ADC(2)}}\ . \tag{5}$$

$R-C$ is the total contribution to the DIP beyond the FO level of approximation, i.e., the relaxation and correlation contributions accounted for in the ADC(2) scheme. In Table VI we report the resulting values for the Si single-center double-core-hole states of silane and tetrafluorosilane. The repulsion-exchange energies of these states are reported as well. The $E_{\mathrm{RE}}$ terms have been computed with the aid of the formulas given in Table V. As one immediately notices from Table VI, the strong repulsion of the core holes overcompensates the energy lowering effect of the relaxation term and, consequently, shifts the DIP's to higher energies. It is worth noting that the repulsion amounts to about four times the size of the relaxation when detaching two electrons out of the strongly localized 1$s$ core orbital. The overall large orbital energy gap between the Si(1$s^{-2}$)- and Si(1$s^{-1}$2$s^{-1}$)-type states is further enlarged to roughly 1850 eV in both systems. For the other states we find the ratios between the repulsion-exchange and many-body contributions to be of the order of 2. These values are comparable to those reported recently for methane and acetylene.[2(a)]

The repulsion-exchange energies simplify for two-center double core vacancies. In the case of two-center states the exchange integrals are negligible for localized orbitals like core orbitals because they describe a short-range interaction. The fact that the holes are indeed situated at different atoms manifests itself in the near degeneracy of corresponding singlet and triplet states (see Table IV). The repulsion-exchange energy reduces to the repulsion term for two-center states and can thus be described to a good approximation by the inverse of the distance between the centers.

To compute relaxation energies we have performed ΔSCF calculations on some double core vacancies in Si$X_4$ ($X$=H,F). There is a lack of experience in SCF computa-

TABLE VI. Many-body contributions and repulsion-exchange energies of single-center double-core-vacancy states in silane and tetrafluorosilane.

| | | | Silane | | | Tetrafluorosilane | | |
|---|---|---|---|---|---|---|---|---|
| No. | Specification[a] | State | Many-body contribution[b] (eV) | Repulsion-exchange energy (eV) | Dominant $2h$ component | Many-body contribution[b] (eV) | Repulsion-exchange energy (eV) | Dominant $2h$ component |
| 1 | $\mathrm{Si}(1s^{-2})$ | $^1A_1$ | 52.71 | 229.73 | $1a_1^{-2}$ | 50.73 | 229.74 | $1a_1^{-2}$ |
| 2 | $\mathrm{Si}(1s^{-1}2s^{-1})$ | $^1A_1$ | 34.59[c] | 66.73 | $1a_1^{-1}2a_1^{-1}$ | 32.61[c] | 66.74 | $1a_1^{-1}3a_1^{-1}$ |
| 3 | $\mathrm{Si}(1s^{-1}2s^{-1})$ | $^3A_1$ | 35.43[c] | 56.79 | $1a_1^{-1}2a_1^{-1}$ | 33.26[c] | 56.80 | $1a_1^{-1}3a_1^{-1}$ |
| 4 | $\mathrm{Si}(1s^{-1}2p^{-1})$ | $^1T_2$ | 36.60 | 68.65 | $1a_1^{-1}1t_2^{-1}$ | 34.29 | 68.64 | $1a_1^{-1}2t_2^{-1}$ |
| 5 | $\mathrm{Si}(1s^{-1}2p^{-1})$ | $^3T_2$ | 36.98 | 62.82 | $1a_1^{-1}1t_2^{-1}$ | 34.76 | 62.81 | $1a_1^{-1}2t_2^{-1}$ |
| 6 | $\mathrm{Si}(2s^{-2})$ | $^1A_1$ | 22.07[c] | 43.76 | $2a_1^{-2}$ | 20.12[c] | 43.76 | $3a_1^{-2}$ |
| 7 | $\mathrm{Si}(2s^{-1}2p^{-1})$ | $^1T_2$ | 21.71* | 53.88 | $2a_1^{-1}1t_2^{-1}$ | d* | 53.88 | $3a_1^{-1}2t_2^{-1}$ |
| 8 | $\mathrm{Si}(2s^{-1}2p^{-1})$ | $^3T_2$ | 21.55* | 35.94 | $2a_1^{-1}1t_2^{-1}$ | d* | 35.94 | $3a_1^{-1}2t_2^{-1}$ |
| 9 | $\mathrm{Si}(2p^{-2})$ | $^1A_1$ | 26.28 | 55.31 | $1t_2^{-2}$ | 24.30 | 55.30 | $2t_2^{-2}$ |
| 10 | $\mathrm{Si}(2p^{-2})$ | $^1E$ | 23.94 | 44.99 | $1t_2^{-2}$ | 21.97 | 47.56 | $2t_2^{-2}$ |
| 11 | $\mathrm{Si}(2p^{-2})$ | $^1T_2$ | 23.94 | 47.57 | $1t_2^{-2}$ | 21.97 | 47.56 | $2t_2^{-2}$ |
| 12 | $\mathrm{Si}(2p^{-2})$ | $^3T_1$ | 24.30 | 42.41 | $1t_2^{-2}$ | 22.36 | 42.40 | $2t_2^{-2}$ |

[a] The specification is given with respect to the parent orbitals of silicon.

[b] The many-body contributions are dominantly characterized by relaxation effects. Otherwise the value is marked by an asterisk.

[c] The value was extracted from an ADC(2) calculation using a core space not including the $2p$ orbital of silicon, i.e., here the Si($2p$) orbital was attributed to the valence space.

[d] The ADC(2) calculation was not fully converged but allows us to estimate the many-body contributions: for the $^1T_2$ and $^3T_2$ states the values range from 15 to 16 eV.

tions on doubly core-ionized states. The computations tend to collapse variationally during the SCF procedure. To understand this fundamental limitation of the SCF we consider, for instance, the $\mathrm{Si}(1s^{-1}2s^{-1})$-derived states of $A_1$ symmetry. These lie higher in energy than other states of the same symmetry. Representatives are the $(1a_1^{-1}3a_1^{-1})$- and $(2a_1^{-1}3a_1^{-1})$-derived states in $\mathrm{SiH_4}^{2+}$ and $(1a_1^{-1}4a_1^{-1})$-, $(1a_1^{-1}5a_1^{-1})$-, $(3a_1^{-1}4a_1^{-1})$-, and $(3a_1^{-1}5a_1^{-1})$-derived states in $\mathrm{SiF_4}^{2+}$, being all of $A_1$ symmetry. Consequently, it is variationally difficult for the HF method to access the higher-lying $\mathrm{Si}(1s^{-1}2s^{-1})$-type states. By variational collapse the SCF procedure converges to lower-lying states of the same symmetry. The favorites are the $(2a_1^{-1}3a_1^{-1})$- and $(3a_1^{-1}4a_1^{-1})$-type states in the case of $\mathrm{SiH_4}$ and $\mathrm{SiF_4}$, respectively. Therefore, we have determined the required HF energies *approximately* as quasistationary energies corresponding to the energy plateaus formed as a function of the iteration number during the SCF procedure. It is thus clear that the results must be considered with care.

In Table VII we report the ΔSCF binding energies of the three single-center singlet-triplet pairs possible in $\mathrm{SiH_4}$. For the $^3A_1$ states the ΔSCF binding energies are smaller by about 10 eV than the corresponding ADC(2) values. Discrepancies of this magnitude are to be expected when relating them to the values of 12.11 and 12.42 eV for methane and acetylene, respectively.[2(a)] These discrepancies are partly due to correlation effects included in the ADC(2) results and partly due to the incomplete relaxation energy in the ADC(2) scheme. Since the removal of two core electrons is connected with strong relaxation effects, we cannot expect a second-order scheme to fully account for these effects. We can expect that the relative energies of the various states are correctly reproduced by the ADC(2). An interesting example is reported in Sec. V B.

As long as the relaxation contributions are the dominant many-body contributions, the ΔSCF procedure is expected to yield smaller DIP's than the ADC(2) ones. The values of the DIP's obtained at the ΔSCF level for

TABLE VII. Binding energies of some single-center double-core-vacancy states of silane and tetrafluorosilane computed by ΔSCF. The corresponding ADC(2) values are given in Tables II and III.

| | | | $\gamma^{\mathrm{DIP}}$ (eV) | |
|---|---|---|---|---|
| No. | Specification[a] | State | Silane | Tetrafluorosilane |
| 1 | $\mathrm{Si}(1s^{-1}2s^{-1})$ | $^1A_1$ | 2050.59 | 2064.07 |
| 2 | $\mathrm{Si}(1s^{-1}2s^{-1})$ | $^3A_1$ | 2048.88 | 2063.01 |
| 3 | $\mathrm{Si}(1s^{-1}2p^{-1})$ | $^1T_2$ | 2018.94 | 2031.76 |
| 4 | $\mathrm{Si}(1s^{-1}2p^{-1})$ | $^3T_2$ | 2014.06 | 2027.21 |
| 5 | $\mathrm{Si}(2s^{-1}2p^{-1})$ | $^1T_2$ | 320.39 | 336.08 |
| 6 | $\mathrm{Si}(2s^{-1}2p^{-1})$ | $^3T_2$ | 304.44 | 316.70 |

[a] The specfication is given with respect to the parent orbitals of silicon.

the last four states in Table VII are larger than the corresponding ADC(2) values. We take this as a possible indication that the ΔSCF procedure as described above has not fully "converged" for these states.

### B. The interesting problem of singlet-triplet separation

The singlet-triplet splittings of the Si$(1s^{-1}2s^{-1})$ double vacancies in $SiH_4$ and $SiF_4$ lead to an interesting problem typical for multiple vacancies. As can be seen in Table II, these splittings are large and amount to nearly 11 eV at the ADC(2) level. In sharp contrast to this result, the SCF calculations predict much smaller splittings of less than 2 eV (see Table VII) as typical for doubly ionized valence states. This strong deviation calls for further analysis. For this purpose we have computed the splittings for several singlet-triplet pairs of $SiX_4{}^{2+}$ ($X=$H,F) by different methods. Our results are collected in Table VIII showing singlet-triplet separations computed via ΔSCF, at the FO level of approximation and by ADC(2). The discrepancies found for the singlet-triplet separations of the Si$(1s^{-1}2p^{-1})$- and Si$(2s^{-1}2p^{-1})$-derived states range from 0.2 to 3.1 eV, as expected from the different levels of theory employed.

The singlet-triplet separation of the Si$(1s^{-1}2s^{-1})$ double vacancies obtained at the SCF level might be a result of a third-order effect and, hence, not reflected by the second-order ADC results. Otherwise it could be an artifact of the not "fully" converged SCF calculations performed or a deficiency inherent in the SCF procedure itself. As a first step towards the understanding of what happens at the SCF level, we have computed the Coulomb and exchange integrals of the 1*s* and 2*s* core orbitals using either nonrelaxed or relaxed molecular orbitals (MO's). In the latter case we have performed two computations using the relaxed MO's of the dicationic singlet and triplet states. Comparing the resulting integrals to those obtained with the MO's of the neutral ground state, the largest change (decrease) is found for the exchange interaction $V_{1s,2s,2s,1s}$ when using the MO's of the Si$(1s^{-1}2s^{-1})$ singlet state. By contrast, it decreases only slightly when computing it with the MO's of the corresponding triplet state. We take these findings as a first indication that the singlet (and not the triplet) states show the extraordinary behavior at the SCF level.

The coupling system of two holes is closely related to that of two electrons. This leads immediately to the idea of analyzing the problem by studying a two-electron model system where the problem simplifies and thus allows us to carry out a more transparent discussion. We have chosen the $Si^{12+}$ ion as a model system in order to investigate the coupling of the two electrons in the 1*s* and 2*s* orbitals of the same atom. For convenience, the singlet configurations of $Si^{12+}$ that are of relevance in this context are denoted by $|\psi_0^S(1s^2)\rangle$, $|\psi_1^S(1s^1 2s^1)\rangle$, and $|\psi_2^S(2s^2)\rangle$ and the triplet configuration by $|\psi^T(1s^1 2s^1)\rangle$. In the SCF the energy of $|\psi_1^S(1s^1 2s^1)\rangle$ is *not* invariant to a mixing of the 1*s* and 2*s* orbitals and is thus lowered by this mixing. Now it becomes clear what happens at the SCF level. Due to the different types of configurations, the SCF procedure on $|\psi_1^S(1s^1 2s^1)\rangle$ (open-shell case) does not variationally collapse to $|\psi_0^S(1s^2)\rangle$ characterized by a closed-shell HF determinant. Based on a variational concept, the SCF procedure tries to mimic the energetically lower lying $|\psi_0^S(1s^2)\rangle$ by artificially contracting the 2*s* orbital.

In this context it is interesting to study how the mixing leads to the artificial energy lowering. Upon the 1*s*-2*s* orbital mixing the singlet wave function $\psi_1^S(1s^1 2s^1)$ gets some $\psi_0^S(1s^2)$ character [constrained by the equal-weight appearance of $\psi_2^S(2s^2)$]. The relevant interaction between the configurations $|\psi_1^S(1s^1 2s^1)\rangle$ and $|\psi_0^S(1s^2)\rangle$ reads

$$H_{10}=\langle \psi_1^S|\hat{H}|\psi_0^S\rangle=\sqrt{2}(h_{2s,1s}+V_{2s,1s,1s,1s})\ ,$$

where $h_{2s,1s}$ is the one-particle matrix element of the 2*s* and 1*s* orbitals and

$$V_{2s,1s,1s,1s}=\langle 2s(1)1s(2)||\mathbf{r}_1-\mathbf{r}_2|^{-1}|1s(1)1s(2)\rangle\ .$$

TABLE VIII. Singlet-triplet splittings ($\Delta_{S\text{-}T}$) of single-center double-core-hole states of silane and tetrafluorosilane computed by ΔSCF. The corresponding values obtained at the frozen orbital (FO) level of approximation and those resulting from ADC(2) calculations are also reported.

| | | | $\Delta_{S\text{-}T}$ (eV) | | |
|---|---|---|---|---|---|
| No. | Specification[a] | States | ΔSCF | FO | ADC(2) |
| | | $SiH_4$ | | | |
| 1 | Si$(1s^{-1}2s^{-1})$ | $^1A_1$-$^3A_1$ | 1.71 | 9.94 | 10.77[b] |
| 2 | Si$(1s^{-1}2p^{-1})$ | $^1T_2$-$^3T_2$ | 4.88 | 5.83 | 6.21 |
| 3 | Si$(2s^{-1}2p^{-1})$ | $^1T_2$-$^3T_2$ | 15.95 | 17.94 | 17.78 |
| | | $SiF_4$ | | | |
| 1 | Si$(1s^{-1}2s^{-1})$ | $^1A_1$-$^3A_1$ | 1.74 | 9.94 | 10.59[b] |
| 2 | Si$(1s^{-1}2p^{-1})$ | $^1T_2$-$^3T_2$ | 4.55 | 5.83 | 6.29 |
| 3 | Si$(2s^{-1}2p^{-1})$ | $^1T_2$-$^3T_2$ | 19.38 | 17.94 | 21[c] |

[a] The specification is given with respect to the parent orbitals of silicon.

[b] The value was extracted from ADC(2) computations using a (1*s*2*s*) space as core orbital space. For details see the text.

[c] The value was taken from not fully converged ADC(2) calculations.

Using the HF orbitals of $|\psi_1^S(1s^1 2s^1)\rangle$, the (absolute) coupling $|H_{10}|$ is computed to reach the enormous size of 533.18 eV. As expected in light of the above discussion, the driving force of this artificially large coupling between the singlet configurations is $|h_{2s,1s}|$, which amounts to 379.03 eV and results from the strong $1s$-$2s$ orbital mixing in $|\psi_1^S(1s^1 2s^1)\rangle$. In the SCF calculation on $|\psi_1^S\rangle$ this surprisingly enormous coupling to $|\psi_0^S\rangle$ is not accounted for. Its neglect leads, in spite of the large energy gap of 1757.88 eV between the 1$s$ and 2$s$ orbitals, to a substantial lowering of the singlet energy and thus to a much too small singlet-triplet splitting of 1.99 eV. The exact singlet-triplet separation has been computed to be 14.01 eV. These SCF and exact results on $\mathrm{Si}^{12+}$ compare favorably well with the ΔSCF and ADC(2) results, respectively, on the corresponding dicationic states of $\mathrm{SiH}_4$ and $\mathrm{SiF}_4$ (see Table VIII).

Obviously, the appearance and strength of $|H_{10}|$ depend on the choice of the orbital basis. If $H_{10}$ is calculated with the MO's of $|\psi^T(1s^1 2s^1)\rangle$ we obtain a positive value of 20.79 eV. Expressing finally the singlet wave functions in the MO basis of $|\psi_0^S(1s^2)\rangle$, the coupling $|H_{10}|$ vanishes, of course, according to Brillouin's theorem. Thus we can conclude that the large size of $|H_{10}|$ is an artifact of the SCF procedure itself and an extension to the multiconfiguration (MC) SCF approach is needed to describe $|\psi_1^S(1s^1 2s^1)\rangle$ correctly. Such an extension should at least comprise the two configurations $|\psi_1^S\rangle$ and $|\psi_0^S\rangle$. The triplet state $|\psi^T\rangle$ is not affected by the above points, the SCF energy is invariant to a mixing of the 1$s$ and 2$s$ orbitals, and the SCF procedure is an appropriate tool. These conclusions have been supported by full-configuration-interaction computations performed on all the relevant states of $\mathrm{Si}^{12+}$.

We conclude that, in contrast to the singlet double core vacancies, the binding energies of the triplet $\mathrm{Si}(1s^{-1}2s^{-1})$ vacancies can be assumed to be reliably predicted by the ΔSCF procedure. We wish to point out that ΔSCF results on double or multiple vacancies deserve, as illustrated here, to be treated with some caution. A more detailed analysis of these limitations of the SCF approach will be presented in a separate article.[24]

### C. Relationship between single and double vacancies

A wide variety of experimental and theoretical studies have been devoted to single core vacancies in electronic systems,[1] but only little is known about double or multiple holes in their cores. Therefore it is convenient to use the results on singly ionized states as a basis for the discussion of the more complex case of double core holes.

Let us consider the relaxation process taking place upon creation of single and double core vacancies and compare the corresponding relaxation energies. In analogy to Eq. (4), the relaxation energy of a single core vacancy $a^{-1}$ is defined by the difference

$$R(a^{-1}) = -\mathcal{V}_{\Delta\mathrm{SCF}}^{\mathrm{IP}} - \varepsilon_a \ , \tag{6}$$

where $\mathcal{V}_{\Delta\mathrm{SCF}}^{\mathrm{IP}}$ is the ionization potential computed by the ΔSCF procedure. Here the ground-state orbital energy $-\varepsilon_a$ of the core orbital $\phi_a$ corresponds to the binding energy obtained at the FO level of approximation. Via perturbation theory one obtains the following approximate second-order expressions for the relaxation energy of a single and double core vacancy, assuming the separability of core and valence electrons:[3]

$$R(a^{-1}) = 2\sum_{j,n} \frac{V_{ajan}^2}{\varepsilon_j - \varepsilon_n} \ , \tag{7}$$

$$R(a^{-1}b^{-1}) = 2\sum_{j,n} \frac{(V_{ajan} + V_{bjbn})^2}{\varepsilon_j - \varepsilon_n} \ . \tag{8}$$

The indices $n$ and $j$ refer to doubly occupied valence orbitals and unoccupied orbitals, respectively. To reveal the relation between $R(a^{-1})$ and $R(a^{-1}b^{-1})$ we express $R(a^{-1}b^{-1})$ in terms of $R(a^{-1})$. For the special case $a=b$, the double vacancy relaxation energy takes on the simple form (in second-order perturbation theory)

$$R(a^{-2}) = 4R(a^{-1}) \ . \tag{9}$$

In the general case $a \neq b$ we crudely estimate the relaxation energy defined in Eq. (8) by

$$R(a^{-1}b^{-1}) \simeq R(a^{-1}) + R(b^{-1}) + 2[R(a^{-1})R(b^{-1})]^{1/2} \ . \tag{10}$$

According to Eq. (9) we may expect the relaxation energy for a double vacancy $a^{-2}$ to equal four times that of a single vacancy $a^{-1}$. A point-charge model where the relaxation energy is quadratic in the hole charge agrees with this second-order result.

To assess how the above findings match in the present case of the $\mathrm{Si}X_4$ ($X=\mathrm{H,F}$) molecules we have computed the relaxation energies of 1$s$ and 2$s$ single and double core vacancies. The relaxation energies $R(a^{-1})$ have been obtained by Eq. (6), while we have determined the values of $R(a^{-2})$ from ADC(2) and Eq. (5), assuming $R \gg |C|$ in the latter. Our results are collected in Table IX repeating the $R(a^{-2})$ terms of Table VI for comparison. A look at the last column of Table IX, which shows the ratios between the relaxation energies, reveals smaller values than predicted by Eq. (9). As discussed in Sec. V A, these discrepancies partly result from correlation effects included in the ADC(2) scheme and from the incomplete account of relaxation energy by ADC(2). In general, the ratio of 4 predicted by second-order perturbation theory is expected to be somewhat too large.

Of course, it is more appropriate to compare relaxation energies obtained at the same level, e.g., computed via the ΔSCF procedure. For the triplet states derived from the $\mathrm{Si}(1s^{-1}2s^{-1})$ configuration it is reasonable to assume that the ΔSCF procedure yields reliable DIP values (see Sec. V B) and, therefore, we consider these states as examples for the general case $a \neq b$. With the $\mathcal{V}_{\Delta\mathrm{SCF}}^{\mathrm{DIP}}$ values and Eq. (4) we obtain relaxation energies of 45.94 and 41.97 eV for the ${}^3A_1$ states of $\mathrm{SiH}_4{}^{2+}$ and $\mathrm{SiF}_4{}^{2+}$, respectively. Equation (10) predicts relaxation energies of 49.52 and 45.49 eV and thus a chemical effect of 4 eV due to the substitution of H by F in agreement with the ΔSCF value.

TABLE IX. Relaxation energies of singly and doubly ionized 1*s* and 2*s* core holes and their ratios for silane and tetrafluorosilane. The relaxation energies $R(a^{-1})$ of the singly core-ionized states and the relaxation energy $R(a^{-1}b^{-1})$ of the triplet $\mathrm{Si}(1s^{-1}2s^{-1})$ states have been computed by the ΔSCF procedure. The relaxation energies $R(a^{-2})$ of the doubly core-ionized states are computed via ADC(2) assuming that the correlation contributions can be neglected and they are, thus, only approximate. All energies are in electron volts.

| | $R(a^{-1})$ | | $R(a^{-1}b^{-1})$ | $R(a^{-2})/R(a^{-1})$ |
|---|---|---|---|---|
| | | $SiH_4$ | | |
| $\mathrm{Si}(1s^{-1})$ | 19.95 | $\mathrm{Si}(1s^{-2})$ | 52.71 | 2.6 |
| $\mathrm{Si}(2s^{-1})$ | 6.61 | $\mathrm{Si}(2s^{-2})$ | 22.07 | 3.3 |
| | | $\mathrm{Si}(1s^{-1}2s^{-1})$ | 45.94 (49.52)[a] | |
| | | $SiF_4$ | | |
| $\mathrm{Si}(1s^{-1})$ | 18.17 | $\mathrm{Si}(1s^{-2})$ | 50.73 | 2.8 |
| $\mathrm{Si}(2s^{-1})$ | 6.16 | $\mathrm{Si}(2s^{-2})$ | 20.12 | 3.3 |
| | | $\mathrm{Si}(1s^{-1}2s^{-1})$ | 41.97 (45.49)[a] | |

[a] The values in parentheses show the prediction of Eq. (10).

### D. Brief comparison with experiment on double-core-excited states

In order to find out where the ADC(2) results on the double core vacancies lie on an absolute energy scale it would be illuminating to compare them to experimental data. Lacking experiments on double core holes in $SiX_4$ ($X=\mathrm{H,F}$), we relate them to the experimental results obtained on double-core-excited states of these molecules.[7] In the photoabsorption spectrum of silane, two groups of signals have been observed with centers at 1973.8 and 1980.3 eV.[7] They have been interpreted as originating from a simultaneous excitation of Si(1*s*) and Si(2*p*) core electrons into low-lying unoccupied orbitals $v^*$ and assigned to a triplet and a singlet state, respectively. In the spectrum of $SiF_4$ the corresponding states have been found to lie at 1984.0 (triplet) and 1990.9 eV (singlet). A further group of peaks centered at 2013.9 eV has been observed and also assigned to the $\mathrm{Si}(1s^{-1}2p^{-1}v^{*2})$ type of states but with another occupation pattern in the orbitals ($v^*$). The multiplicity of the resulting states has not been specified. For the Si(1*s*2*s*) double-excitation process a single experimental value for $SiF_4$ around 2027 eV is reported. From these experiments (the energies of the double-core-excited states converge to the DIP's), the DIP's of the associated double core vacancies have been predicted to lie 25 eV above the excitation energies of the observed double-core-excited states.[7]

Due to the higher amount of experimental data on $\mathrm{Si}(1s^{-1}2p^{-1}v^{*2})$ electron excitations we focus on $\mathrm{Si}(1s^{-1}2p^{-1})$-derived states. It is clear that the binding energies of doubly core-excited states cover an energy region depending on the occupation pattern of the virtual orbitals $v^*$. According to Ref. 7, the experimental data on the Si(1*s*2*p*) doubly excited states are spread over a range of nearly 30 eV in $SiF_4$. For a preliminary comparison we focus on the signals common to the spectra of both molecules, i.e., we exclude the group observed for $SiF_4$ at 2013.9 eV. Adding 25 eV to the experimental data[7] we obtain, on the average, a deviation of 14 eV from the corresponding ADC(2) values. This finding is in line with the result on the $\mathrm{Si}(1s^{-1}2s^{-1})$-derived triplet state, where we have found a deviation of about 10 eV between the ΔSCF and ADC(2) values (see Sec. V A). We recall that the absolute DIP values of the $\mathrm{Si}(1s^{-1}2p^{-1})$-derived states are of the order of 2000 eV and a discrepancy of the above-mentioned magnitude is indeed a satisfactory result.

A guide to assess the relative accuracy of the ADC(2) results are the singlet-triplet splittings. Extracting the singlet-triplet splits of the $\mathrm{Si}(1s^{-1}2p^{-1})$-derived states from the experimental data, they amount to 6.5 and 6.9 eV in $SiH_4$ and $SiF_4$, respectively, while they are computed to be 6.21 and 6.29 eV according to ADC(2) (see Table VIII). Obviously, the literature results and ours match well, confirming that relative binding energies are described quite accurately by the second-order ADC scheme, even in the case of doubly core-ionized states.

Finally, we mention a minor point. In order to achieve coincidence with experiment, the data of a semiempirical model had to be shifted down in energy by several electron volts.[7] This shift can be explained readily. As is immediately seen from Eq. (10), it is not sufficient to consider single-hole-relaxation effects [$R(a^{-1})$ and $R(b^{-1})$] as done by using experimentally determined single-ionization potentials. A relevant contribution [third term on the rhs of Eq. (10)] to the excitation energy must be included as well which, according to Eq. (10), can also be estimated from the single-ionization potentials. The lacking term is computed to amount to 23 and 21.2 eV for the $\mathrm{Si}(1s^{-1}2s^{-1})$ double ionization in $SiH_4$ and $SiF_4$, respectively.

## VI. SUMMARY AND CONCLUDING REMARKS

In the present work we have investigated theoretically the double vacancies in the core of silane and tetrafluorosilane, using the Green's-function method. Within the computations we have imposed the separability of core and valence electrons and extended the core space for the first time to include more than a single orbital. It has been shown that for most purposes the core-valence separation remains a good approximation even for an extended core orbital space. Because of the localized nature of the core orbitals the double-vacancy states have been found to cluster in distinct groups according to the relative location of the two holes. One finds dicationic single-center states where the vacancies are located in the same or different core orbitals of the same atom as well as two-center states where the holes are on different atoms. In the latter case a further clustering of states with similar orbital hole distribution character has been observed.

The binding energies of the double-core-hole states in $SiH_4$ and $SiF_4$ have been analyzed in terms of hole-hole interaction and many-body effects. For all single-center states, except the $Si(1s^{-2})$ double vacancies, the hole-hole interaction effects have been computed to amount approximately to twice the size of the many-body contributions. The hole-hole interactions consisting of the hole-hole repulsion and exchange terms have been shown to be mainly determined by the electrostatic repulsion between the holes. The many-body contributions comprise the relaxation and correlation effects and are, as expected for core vacancies, dominated by the relaxation of the valence electrons. For particular types of double-core-hole states, however, correlation contributions also play a substantial role. Our ADC(2) computations predict the existence of a variety of dicationic satellite states, indicating the possibility of a breakdown of the molecular-orbital picture of double ionization in *core*-vacancy situations also.

To compute relaxation energies we have performed ΔSCF calculations on some double core vacancies in $SiX_4$ ($X=$H,F) and encountered an interesting problem of the singlet-triplet separation that should be typical for multiple vacancies. By studying a two-electron model system we could show beyond doubt that the binding energies of the singlet $Si(1s^{-1}2s^{-1})$ vacancies are not correctly described at the SCF level due to an artifact of the ΔSCF procedure itself, and that an extension to a MCSCF approach is needed. The binding energies of the corresponding triplet holes, on the other hand, can be assumed to be reliably predicted by the ΔSCF. As a major result, we would like to stress that, apart from errors in the absolute binding energies of some dicationic states, the DIP's relative to each other may also be affected by these limitations of the SCF method and hence ΔSCF results on double or multiple vacancies should generally be considered with care.

For double core vacancies the analysis has exhibited several advantages of the ADC(2) scheme compared to the ΔSCF procedure. In contrast to ΔSCF, the relative energy positions of the doubly core-ionized states can be assumed to be satisfactorily described by ADC(2). This finding has been substantiated by relating the ADC(2) results to those extracted from experiments on doubly core-excited states.[7] In addition to the above-mentioned limitations of the SCF approach, the SCF computations on double core holes have shown that it is variationally difficult for the HF method to describe the corresponding states and, in particular, to access higher-lying double-core-vacancy states in the presence of lower-lying dicationic states of the same symmetry. The Green's-function ADC theory offers the possibility of *directly* computing the binding energies of *all* dicationic states of interest at a time that drastically reduces the numerical effort compared to ΔSCF.

Because of the lack of experience on multiple core vacancies we have paid attention to their relation to the well-investigated single core vacancies. In particular, the comparison of the corresponding relaxation energies allows us to obtain a further understanding of double core vacancies. Calculations have been performed on both single-core and double-core-vacancy states and explicit expressions for the respective binding energies are given in second-order perturbation theory. Another aspect of interest is the possible decay of a double core vacancy in comparison to that of a single core vacancy, in particular, when the core space comprises several orbitals as in the present cases of $SiX_4$ ($X=$H,F). In analogy to the Auger decay, a double-core-hole state may decay into triply ionized states by emission of a further electron. In addition to this mechanism, similar to that of a single core hole, a variety of radiative and nonradiative decay channels exist for a double core vacancy that are not present in the case of a single core vacancy. We therefore expect in general the appearance of much more pronounced and complex shake-up and shake-off structures in double core than in single-core-hole situations. In fact, we see that the detachment of two core electrons is of interest by itself because it is accompanied by several *additional* effects not found when removing only one core electron.

Up to now much less attention has been paid to the study of the nuclear dynamics in a double-core-vacancy states. Because of the near degeneracy of some doubly core-ionized states, in particular, that observed for two-center dicationic states of a molecule with several equivalent atoms like $SiF_4$, the coupling of the states through the nuclear motion should lead to comparably interesting vibronic coupling phenomena, as found for doubly ionized valence states.[14]

We hope that our theoretical results on double core holes will stimulate experiments on double-core-vacancy states as well as further experimental activities in the field of double-core-excited states.

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[1] See, for example, Proceedings of the Fourth International Conference on Electron Spectroscopy, edited by C. R. Brundle, G. E. McGuire, and J. J. Pireaux [J. Electron Spectrosc. Relat. Phenom. **51&52** (1990)].

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