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Contributions from Atomic p(Se), d(Se), and f(Se) Orbitals to Absolute Paramagnetic Shielding Tensors in Neutral and Charged SeH$_n$ and Some Oxides Including the Effect of Methyl and Halogen Substitutions on σ^p(Se)

Waro Nakanishi,*[a] Satoko Hayashi,[a] Kenji Narahara,[a] and Masahiko Hada[b]

Abstract: Contributions from atomic p(Se), d(Se), and f(Se) orbitals to σ^p(Se) are evaluated for neutral and charged Se*H$_n$ (* = null, +, or −) and some oxides to build the image of the contributions. The effect of methyl and halogen substitutions is also examined employing R$_r$Se*X$_x$O$_o$ (* = null, +, or −) where R = H or Me; X = F, Cl, or Br. The p(Se) contributions are larger than 96 % for SeH$^-$ ($C_{\infty v}$), SeH$_2$ (C_{2v}), SeH$_3^+$ (C_{3v}), SeH$_3^+$ (D_{3h}), and SeH$_4$ (T_d). Therefore, σ^p(Se) of these compounds can be analyzed based on p(Se). The p(Se) contributions are 79–75 % for SeH$_4$ (TBP), SeH$_5^+$ (TBP), SeH$_5^+$ (SP), and SeH$_5^-$ (SP). Methyl and halogen substitutions increase the contributions by 1–2 % (per Me) and 4–7 % (per X), respectively. The contributions are 92–79 % for H$_2$SeO (C_s), H$_2$SeO$_2$ (C_{2v}), and H$_4$SeO (C_{2v}). The values are similarly increased by the substitutions. Consequently, σ^p(Se) of these compounds can be analyzed based on p(Se) with some corrections by d(Se). The p(Se) contribution of SeH$_6$ (O_h) is 52 %: σ^p(Se: SeH$_6$ (O_h)) must be analyzed based on both p(Se) and d(Se). The contributions for the Me and X derivatives of SeH$_6$ amount to 86–77 %. Therefore, σ^p(Se) of the derivatives can also be analyzed mainly based on p(Se) with some corrections by d(Se). Contributions from f(Se) are negligible. Contributions from 4p(Se) in vacant orbitals are also considered. A utility program derived from the Gaussian 03 (NMRANAL-NH03G) is applied to evaluate the contributions.

Keywords: ab initio calculations · absolute shielding tensors · NMR spectroscopy · selenium

Introduction

Selenium-containing compounds show versatile reactivities and afford many structurally interesting compounds.[1,2] Atomic 4p(Se) orbitals essentially control the reactivities and the fine structures of the compounds, since selenium is a member of the Group 16 elements. Atomic 4d(Se) orbitals play an additional role in low-coordinated selenium compounds but the importance becomes larger in higher coordinated cases.[3,4] ^{77}Se NMR spectroscopy is widely used to study selenium chemistry.[5–8] ^{77}Se NMR chemical shifts (δ(Se)) are utilized to determine the structures of selenium compounds and follow the reactions on a daily basis, since they are highly sensitive to structural changes.[1–10] Atomic 4p(Se) orbitals predominantly determine δ(Se), however, 4d(Se) can play an important role as the oxidation or coordination number at selenium increases.

More information could be derived from δ(Se), which would be useful to investigate physical, chemical, and biological sciences, if they can be analyzed separately by the factors which control the chemical shifts. Plain rules from theory are necessary to determine geometric and electronic structures based on the chemical shifts.[9,10] The rules should be familiar to the experimental chemists. It is informative to employ the absolute paramagnetic shielding tensors (σ^p(Se)) for the analysis of chemical shifts, since the σ^p(Se) values are much more sensitive to the structural changes of selenium compounds and they can be predicted with satisfactory accuracy.[11–13] While $\sigma^p(N)$ is evaluated accurately by the CPHF method,[14,15] we will mainly discuss $\sigma^p(N)$ with an approximated image derived from Equation (1).[16]

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$$\sigma^{p}_{zz}(N) = -(\mu_o e^2/2m_e{}^2)\sum_{i}^{\mathrm{occ}}\sum_{a}^{\mathrm{unocc}}(\varepsilon_a-\varepsilon_i)^{-1} \times\{\langle\psi_i|\hat{L}_z|\psi_a\rangle\langle\psi_a|\hat{L}_{z,N}r_N^{-3}|\psi_i\rangle + \langle\psi_i|\hat{L}_{z,N}r_N^{-3}|\psi_a\rangle\langle\psi_a|\hat{L}_z|\psi_i\rangle\} \quad (1)$$

Very recently, we reported the behavior of electron-population terms ($\langle r_{\mathrm{Se}}^{-3}\rangle_{4\mathrm{p}}$) and demonstrated that the terms serve as the charge factor to determine σ^p(Se).[17,18] To establish the desired rules by using $\langle r_{\mathrm{Se}}^{-3}\rangle_{4\mathrm{p}}$, it is necessary to clarify how the chemical shifts are controlled by atomic p(Se) orbitals, together with d(Se) and f(Se). Contributions from p(Se), d(Se), and f(Se) to σ^p(Se) are examined[19] for various neutral and charged selenium species (Se*H_n: *=null, +, or −; n=1–6) and some oxides [H_nSeO_o: (n,o)=(2,1), (2,2), and (4,1)] to build the image of the contributions. Figure 1 shows the structures of Se*H_n (*=null, +, or −; n=1–6) and H_nSeO_o, examined in this work. They are classified by the numbers of lone pairs (n_{lp}) and ligands (n_{L}) in SeL_n drawn for the compounds. The contributions are also examined for the methyl and halogen derivatives of Se*H_n and H_nSeO_o [R_rSe*$X_x$$O_o$ (*=null, +, or −; R=H or Me and X=H, F, Cl, or Br with r, x=0–6, and o=0–2)]. The differences in the contributions are discussed as the effect of methyl and halogen substitutions on the contributions.

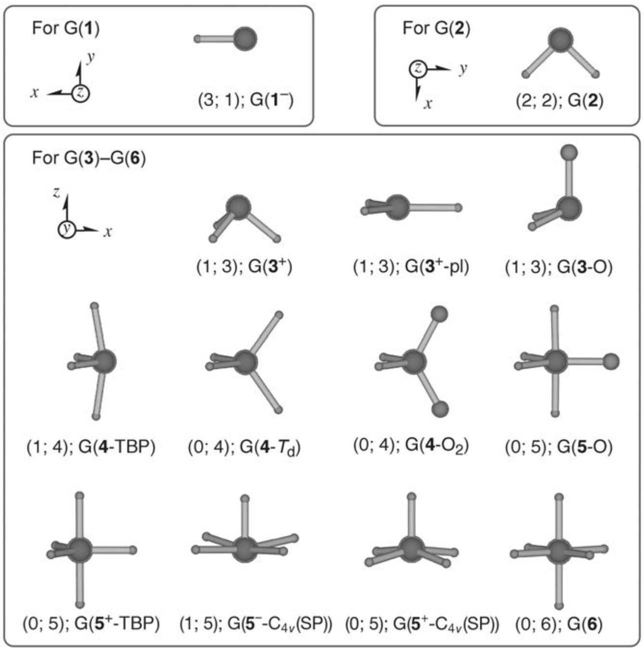

Figure 1. Structures of selenium compounds, Se*H_n (*=null, +, or −) and H_nSeO_o, studied in this work. They are classified by the numbers of the lone pairs (n_{lp}) and ligands (n_{L}) in SeL_n. Optimized structures are employed for the presentation.

Here, we report the contributions from the atomic p(Se), d(Se), and f(Se) orbitals to σ^p(Se) in Se*H_n and R_rSe*$X_x$$O_o$ (*=null, +, or −), where R=H or Me and X=H, F, Cl, or Br. The results will help to understand how p(Se), d(Se), and f(Se) orbitals contribute to σ^p(Se). It is also aimed to develop the standard rules to determine geometric and electronic structures based on chemical shifts founded in theory and familiar to the experimental chemists.

Results and Discussion

Calculation method: The 6-311+G(3df,3pd) basis sets[20,21] in the Gaussian 03 program package[22] are employed for the calculations. Structural optimizations are performed at the density functional theory (DFT) level of the Becke three-parameter hybrid functionals with the Lee–Yang–Parr correlation functional (B3LYP).[23] The gauge-independent atomic orbital method (GIAO)[24] was applied to evaluate absolute magnetic shielding tensors of Se (σ(Se)) at the DFT (B3LYP) level by using the structures optimized with the same method (the GIAO-DFT method). The utility program derived from the Gaussian 03 program are applied to evaluate the contributions from each occupied molecular orbital (ψ_i), occupied MO to occupied or unoccupied MO ($\psi_i \rightarrow \psi_j$ or $\psi_i \rightarrow \psi_a$) transition,[25] and the atomic p(Se), d(Se), and f(Se) orbitals (NMRANAL-NH03G).

Contributions from each MO and p(Se), d(Se), and f(Se) in Se*H_n: The σ^p(Se) values are calculated for Se*H_n (*=null, +, or −) with the DFT-GIAO method employing the 6-311+G(3df,3pd) basis sets. The contributions are evaluated separately by the transitions between occupied MOs (Occ-to-Occ: Occ) and by those from occupied MOs to unoccupied MOs (Occ-to-Unocc). The contributions from Occ-to-Unocc are evaluated further separated by each occupied MO (ψ_i). Table 1 collects the results. The total σ^p(Se) values are given separately by Occ (the $\psi_i \rightarrow \psi_j$ transitions)[26–28] and by Occ-to-Unocc (the $\psi_i \rightarrow \psi_a$ transitions). σ^p(Se) from the $\psi_i \rightarrow \psi_a$ transitions are given by ψ_1–ψ_{14} (inner MOs), and each of ψ_{15}–ψ_{18}, together with ψ_{19} and/or ψ_{20}, if any. The contributions from atomic p(Se), d(Se), and f(Se) orbitals to σ^p(Se) are also shown, together with those at H (χ(H)).

As shown in Table 1, ψ_{19} and/or ψ_{20} appear in Se*H_n for n=4–6. Figure 2 draws ψ_{19} and/or ψ_{20} in Se*H_n (n=4–6). ψ_{19} (HOMO) of SeH_4 (T_d) is mainly constructed by 4s(Se). The main character of ψ_{19} in SeH_4 (TBP) and $SeH_5{}^+$ (TBP) is ψ_2 (3c–4e: three center–four electron bonds) of H_{ap}-Se-H_{ap}, which contain some d character. ψ_{19} of $SeH_5{}^+$ (C_{4v}) and ψ_{19} and ψ_{20} of $SeH_5{}^-$ (C_{4v}) and SeH_6 (O_h) are substantially constructed by 4d(Se).

The contributions from Occ-to-Occ transitions are positive for Se*H_n. All occupied MOs contribute to the Occ-to-Occ transitions. The values will not discuss in more detail herein.[29] The σ^p(Se) values contributed from inner MOs (ψ_1–ψ_{14}) are positive except for SeH^- ($C_{\infty v}$) (−1.3 Hz) and SeH_4 (T_d) (−6.3 Hz), magnitudes of which are very small. Contributions from ψ_{16}–ψ_{18} in Se*H_n are very large, since they are mainly constructed by 4p(Se). Those from ψ_{15} are small, which are mainly constructed by 4s(Se).

As shown in Table 1, the contributions from p(Se) and d(Se) in SeH_2 (C_{2v}) are −906 and −27 ppm, respectively,

Table 1. Contributions from each MO and from atomic p(Se), d(Se), and f(Se) orbitals, together with χ(H), to σ^p(Se) in Se*H_n (*=null, +, or −).[a–c]

Species	Occ[d]	ψ_1–ψ_{14}	ψ_{15}	ψ_{16}	ψ_{17}	ψ_{18}	ψ_{19}	ψ_{20}	σ^p(Se)	p(Se)	d(Se)	f(Se)	χ(H)[e]	% p(Se)
SeH^- ($C_{\infty v}$)	264.0	−1.3	−14.5	−272.0	−238.8	−238.8			−501.5	−496.0	−11.0	0.2	5.3	98.9
SeH_2 (C_{2v})	324.6	0.6	−19.3	−254.4	−365.4	−615.0			−928.8	−906.1	−27.5	−0.4	5.2	97.6
SeH_3^+ (C_{3v})	250.0	9.5	−21.3	−363.2	−363.2	−591.8			−1079.9	−1039.0	−48.1	0.4	6.8	96.2
SeH_3^+ (D_{3h})	224.6	4.3	−1.3	−344.4	−344.5	−613.3			−1074.6	−1029.9	−48.7	−0.6	4.6	95.8
SeH_4 (T_d)	282.5	−6.3	0.1	−647.3	−647.3	−647.3	−1.1[f]		−1666.8	−1629.5	−40.4	0.5	2.6	97.8
SeH_4 (C_{2v})[g]	321.9	13.2	−16.4	−316.1	−359.3	−447.7	−161.9[h]		−966.3	−765.8	−203.7	−0.1	3.3	79.3
SeH_5^+ (D_{3h})[g]	186.9	29.4	0.0	−395.4	−395.4	−417.0	−216.0[i]		−1207.4	−911.4	−294.8	−0.1	−1.1	75.5
SeH_5^+ (C_{4v})[j]	218.8	23.2	−1.6	−420.7	−420.7	−342.3	−216.6[i]		−1159.9	−867.9	−291.3	0.0	−0.8	74.8
SeH_5^- (C_{4v})[j]	410.6	11.0	−16.5	−378.9	−390.7	−390.7	−92.0[i]	−58.6[i]	−905.9	−674.5	−235.6	−0.2	4.3	74.5
SeH_6 (O_h)	326.7	27.9	0.1	−327.5	−327.5	−327.5	−177.9[i]	−177.9[i]	−983.6	−514.1	−467.4	0.2	−2.3	52.3

[a] Calculated with the DFT-GIAO method employing the 6-311+G(3df,3pd) basis sets. [b] A utility program (NMRANAL-NH03G) being employed. [c] In ppm. [d] Contribution from the occupied MOs to occupied MOs transitions. [e] Contribution from AOs at H. [f] Mainly constructed by 4s(Se). [g] Trigonal bipyramidal (TBP). [h] Corresponding to ψ_2 of H_{ax}-Se-H_{ax}. [i] Mainly constructed by 4d(Se). [j] Square pyramidal (SP).

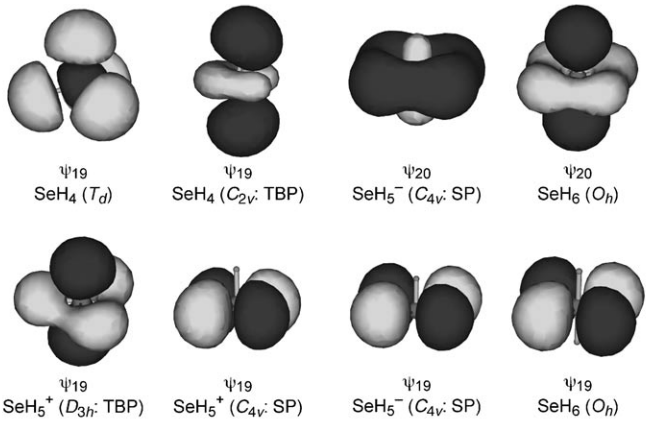
ψ_{19} SeH_4 (T_d)
ψ_{19} SeH_4 (C_{2v}: TBP)
ψ_{20} SeH_5^- (C_{4v}: SP)
ψ_{20} SeH_6 (O_h)
ψ_{19} SeH_5^+ (D_{3h}: TBP)
ψ_{19} SeH_5^+ (C_{4v}: SP)
ψ_{19} SeH_5^- (C_{4v}: SP)
ψ_{19} SeH_6 (O_h)

Figure 2. ψ_{19} and/or ψ_{20} in Se*H_n (*=null, +, or −) for n=4–6.

while those from f(Se) and χ(H) are negligible. The contribution from p(Se) amount to 98 % in SeH_2 (C_{2v}). Similarly, the p(Se) contributions are larger than 96 % for SeH^- ($C_{\infty v}$), (SeH_2 (C_{2v})), SeH_3^+ (C_{3v}), SeH_3^+ (D_{3h}), and SeH_4 (T_d). These compounds have at least one lone-pair orbital at Se ($n_{lp} \geq 1$), except for SeH_4 (T_d). The magnitudes of the contributions from d(Se) are less than −50 ppm (<4 %) in these compounds and the contributions from f(Se) and χ(H) are negligible. The small magnitude of the d(Se) contributions in SeH^- ($C_{\infty v}$), SeH_2 (C_{2v}), SeH_3^+ (C_{3v}), and SeH_3^+ (D_{3h}) with $n_{lp} \geq 1$ can be well explained through the polarization effect of d(Se) in these compounds. ψ_{18} of each compound is HOMO. ψ_{19} (HOMO) of SeH_4 (T_d) is constructed mainly by 4s(Se). Therefore, the contribution from ψ_{19} is negligible, which must be responsible for its large p(Se) contribution, although it has no lone-pair orbitals. The results demonstrate that σ^p(Se) can be analyzed based on p(Se) for SeH^- ($C_{\infty v}$), SeH_2 (C_{2v}), SeH_3^+ (C_{3v}), SeH_3^+ (D_{3h}), and SeH_4 (T_d).

On the other hand, the p(Se) contributions are 79 % for SeH_4 (C_{2v}; TBP: n_{lp}=1) and 75 % for SeH_5^+ (D_{3h}; TBP: n_{lp}=0), SeH_5^+ (C_{4v}; SP: n_{lp}=0), and SeH_5^- (C_{4v}; SP: n_{lp}=1[30]). Contributions from d(Se) amount to about −200 to −300 ppm in these compounds. Such large d(Se) contributions can not be explained by the polarization effect of d(Se). ψ_{19} of SeH_5^+ (SP) and ψ_{19} and ψ_{20} of SeH_5^- (SP) are substantially constructed by 4d(Se). Nevertheless, σ^p(Se) for SeH_4 (TBP), SeH_5^+ (TBP), SeH_5^+ (SP), and SeH_5^- (SP) could be approximately analyzed based on p(Se) with some corrections by d(Se), since the p(Se) contributions are 75–79 %. In the case of SeH_6 (O_h: n_{lp}=0), the p(Se) contribution is 52 % and its ψ_{19} and ψ_{20} are substantially constructed by 4d(Se). Consequently, σ^p(Se) must be analyzed as the contributions from both p(Se) and d(Se) for SeH_6 (O_h).

How do alkyl and halogen substitutions affect on σ^p(Se) in Se*H_n and the oxides? After elucidation of the contributions from p(Se) in Se*H_n, the next task is to clarify the contributions in R_rSe*$X_x$$O_o$ (R=H or Me: X=F, Cl, or Br).

Effect of Me and halogen substitutions on the contributions in R_rSe*$X_x$$O_o$: Contributions from p(Se), d(Se), and f(Se) to σ^p(Se), together with AOs other than those of Se, are also evaluated for R_rSe*$X_x$$O_o$ (*=null, +, or −). Table 2 collects the results for R_rSe*X_x (*=null, +, or −), where R=H or Me, X=F, Cl, or Br. Table 3 shows the contributions from p(Se), d(Se), and f(Se) to σ^p(Se) in R_rSe*$X_x$$O_o$ (*=null, +, or −), where R=H or Me, X=F and o=1 or 2. The differences in σ^p(Se) between R_rSe*$X_x$$O_o$ (o=0–2) and Se*H_n are discussed as the effect of Me and halogens.

As shown in Table 2, the methyl substitution on Se*H_n (*=null, +, or −) leads to a slight increase in the p(Se) contributions (1–2 % per Me).[31] Consequently, σ^p(Se) can be analyzed based on p(Se) for the methyl derivatives of SeH^- ($C_{\infty v}$), SeH_2 (C_{2v}), SeH_3^+ (C_{3v}), SeH_3^+ (D_{3h}), and SeH_4 (T_d). In the case of the fluorine derivatives, the substitution increases considerably the p(Se) contribution (5–7 % per F): The p(Se) contribution increases from 79 % in SeH_4 (TBP) to 92 % in H_2SeF_2 (TBP) then to 94 % in Me_2SeF_2 (TBP). Contributions from p(Se) in Me_2SeCl_2 (TBP) and Me_2SeBr_2 (TBP) are slightly larger than that in Me_2SeF_2 (TBP). The p(Se) contributions of about 95 % in Me_2SeX_2 (TBP) (X=F, Cl, and Br) imply that σ^p(Se) of R_2SeX_2 (TBP) can be analyzed based on p(Se).

How are the p(Se) contributions of about 75 % for SeH_5^+ (TBP: n_{lp}=0), SeH_5^+ (SP: n_{lp}=0), and SeH_5^- (SP: n_{lp}=1[30]) improved by the methyl and fluorine substitutions? The methyl and fluorine substitutions on SeH_5^+ (TBP), SeH_5^+

Table 2. Effect of methyl and halogen substitutions on the contributions of atomic p(Se), d(Se), and f(Se) orbitals, together with AOs of atoms other than Se, to σ^p(Se) in $R_rSe{*}X_x$ (* = null, +, or −).[a–c]

Species	σ^p(Se)	p(Se)	d(Se)	f(Se)	Others	% p(Se)
$SeMe^-$ (C_s)	−1129.1	−1127.4	−13.8	3.0	9.1	99.9
$SeMe_2$ (C_{2v})	−1338.7	−1309.3	−40.8	0.5	10.9	97.8
$SeMe_3^+$ (C_{3v})	−1552.0	−1491.4	−74.3	−0.6	14.3	96.1
$SeMe_3^+$ (C_{3h})	−1226.7	−1163.9	−65.0	−3.9	6.1	94.9
$SeMe_4$ (T_d)	−2174.4	−2133.1	−33.8	3.5	−10.9	98.1
H_2SeF_2 (C_{2v})[d]	−1706.9	−1574.9	−137.0	−2.2	7.1	92.3
Me_2SeF_2 (C_{2v})[d]	−2006.1	−1879.2	−132.1	−1.6	6.8	93.7
Me_2SeCl_2 (C_{2v})[d]	−1730.3	−1629.4	−115.7	−0.6	15.4	94.2
Me_2SeBr_2 (C_{2v})[d]	−1656.1	−1565.7	−103.2	−0.2	13.1	94.5
$Me_3SeF_2^+$(C_{3h})[d]	−2001.5	−1790.4	−202.7	−6.2	−2.2	89.5
SeF_5^+ (C_{3h})[d]	−2133.9	−1879.8	−273.6	−7.9	27.3	88.1
$SeMe_5^+$ (C_s)[e]	−1469.5	−1294.2	−269.3	−3.4	97.4	88.1
SeF_5^+ (C_{4v})[e]	−2154.2	−1891.1	−261.5	−7.3	5.7	87.8
$SeMe_5^-$ (C_s)[e]	−1223.3	−1100.5	−209.2	−2.2	88.5	90.0
SeF_5^- (C_{4v})[e]	−2261.7	−2079.7	−181.4	−3.5	2.9	92.0
$SeMe_6$ (C_i)	−1069.9	−822.8	−378.7	1.0	130.6	76.9
$HSeF_5$ (C_{4v})	−1894.3	−1599.9	−282.7	−3.5	−8.2	84.5
$MeSeF_5$ (C_s)	−1973.5	−1692.6	−271.1	−5.5	−4.3	85.8
SeF_6 (O_h)	−1921.5	−1630.0	−274.0	−4.7	−12.9	84.8

[a] Calculated with the DFT-GIAO method employing the 6-311+G(3df,3pd) basis sets. [b] A utility program (NMRANAL-NH03G) being employed. [c] In ppm. [d] Trigonal bipyramidal (TBP). [e] Square pyramidal (SP).

(SP), and SeH_5^- (SP) similarly increase the p(Se) contributions. The p(Se) contribution of 76% in SeH_5^+ (TBP) increases to 90% in $Me_3SeF_2^+$ (TBP) and to 88% in SeF_5^+ (TBP). Similarly, the p(Se) contributions of 75% in SeH_5^+ (SP) and SeH_5^- (SP) increase to 88% in $SeMe_5^+$ (SP), 90% in $SeMe_5^-$ (SP), and 92% in SeF_5^- (SP) (Table 2). The results show that σ^p(Se) of these compounds can be substantially analyzed based on p(Se), with some corrections by d(Se). Is the low p(Se) contribution of 52% in SeH_6 (O_h: $n_{lp} = 0$) really improved by the methyl and/or fluorine substitutions? The p(Se) contribution increases to 77% in $SeMe_6$ (C_i). The 25% increment in $SeMe_6$ (C_i) corresponds to the 4% per Me.[32] The p(Se) contributions are about 85% for $HSeF_5$ (C_{4v}), $MeSeF_5$ (C_s), and SeF_6 (O_h). The 33% increment is achieved in total, which correspond to the 5–6% improvement per F in these cases. As a result, σ^p(Se) of these compounds can also be analyzed approximately based on p(Se) with some corrections by d(Se).

As shown in Table 3, the p(Se) contributions are 92, 86, and 79% for H_2SeO (C_s: $n_{lp} = 1$), H_2SeO_2 (C_{2v}: $n_{lp} = 0$), and H_4SeO (C_{2v}: $n_{lp} = 0$), respectively. The contributions are increased to 93, 87, and 87% in Me_2SeO (C_s), Me_2SeO_2 (C_{2v}), and Me_2SeF_2O (C_{2v}), respectively. The effect of the methyl and fluorine substitutions in these compounds is essentially the same as that predicted for $Se{*}H_n$, although it is difficult to correlate the selenium compounds containing the Se=O group(s) directly to $Se{*}H_n$. It is demonstrated that σ^p(Se) of $R_rSeX_xO_o$ ($o = 1$ or 2) can be analyzed based on p(Se) with some corrections by d(Se).

Why does the halogen substitution increase the p(Se) contribution that much? The reason is considered employing H_2SeF_2 (TBP) and SeF_6 (O_h).

Contributions from p(Se) in H_2SeF_2 and SeF_6: The reciprocal orbital energy gaps $[(\varepsilon_a - \varepsilon_i)^{-1} = \Delta\varepsilon^{-1}]$ shown in Equation (1) would be a candidate for the reason of the increased p(Se) contributions by the fluorine substitution. The relative values of $\Delta\varepsilon^{-1}$ ($\Delta\varepsilon^{-1}_{rel}$) are examined for SeH_6 (O_h) and SeF_6 (O_h), first.

Figure 3 depicts the main transitions arising from p(Se) and d(Se) in SeH_6 (O_h) and SeF_6 (O_h), together with the $\Delta\varepsilon^{-1}$ and $\Delta\varepsilon^{-1}_{rel}$ values in the transitions. ψ_{16}–ψ_{18} of SeH_6 (O_h) are mainly constructed by 4p(Se), whereas ψ_{19} and ψ_{20} are constructed by 4d(Se) (see also Figure 2). ψ_{16}–ψ_{18} are degenerated with each other and so are ψ_{19} and ψ_{20} in SeH_6 (O_h). ψ_{18} and ψ_{19} contribute to σ^p(Se) by −328 and −178 ppm, respectively (Table 1). Most important transitions in ψ_{18} are $\psi_{18} \rightarrow \psi_{29}$ and $\psi_{18} \rightarrow \psi_{31}$ (−183 ppm for each). Four other transitions from ψ_{16} and ψ_{17} are degenerated to the transitions in SeH_6 (O_h). Consequently, six transitions are degenerated (Table 4). The $\psi_{19} \rightarrow \psi_{26}$ transition (−167 ppm) is the main one in ψ_{19}, which is mainly contributed from 4d(Se). The energy difference between ψ_{18} and ψ_{29} is 0.585 au and that between ψ_{19} and ψ_{26} is 0.339 au. Consequently, $\Delta\varepsilon^{-1}$ in the $\psi_{19} \rightarrow \psi_{26}$ transition (1/0.339 = 2.95) is 1.72 times larger than that in the $\psi_{18} \rightarrow \psi_{30}$ transition (1/0.585 = 1.71). This must be responsible for the large d(Se) contribution to σ^p(Se) in SeH_6 (O_h).

Table 3. Effect of methyl and halogen substitutions on the contribution of atomic p(Se), d(Se), and f(Se) orbitals, together with AOs of atoms other than Se, to σ^p(Se) in H_nSeO_o and $R_rSeX_xO_o$.[a–c]

Species	σ^p(Se)	p(Se)	d(Se)	f(Se)	Others	% p(Se)
H_2SeO (C_s)	−1905.2	−1749.1	−155.3	−2.1	1.2	91.8
Me_2SeO (C_s)	−2098.9	−1946.8	−154.1	−2.1	4.1	92.8
H_2SeO_2 (C_{2v})	−2074.6	−1783.8	−285.4	−4.7	−0.8	86.0
Me_2SeO_2 (C_{2v})	−2203.9	−1924.2	−276.9	−5.4	2.6	87.3
H_4SeO (C_{2v})	−1454.8	−1148.3	−307.4	−1.6	2.5	78.9
H_2SeF_2O (C_{2v})	−1933.0	−1665.3	−263.7	−6.4	2.3	86.1
Me_2SeF_2O (C_{2v})	−2097.1	−1832.0	−247.1	−9.4	−8.7	87.4

[a] Calculated with the DFT-GIAO method employing the 6-311+G-(3df,3pd) basis sets. [b] A utility program (NMRANAL-NH03G) being employed. [c] In ppm.

In the case of SeF_6 (O_h), the $\psi_{28} \rightarrow \psi_{51}$ transition is most important for the p(Se) contribution to σ^p(Se) and the $\psi_{35} \rightarrow \psi_{87}$ transition is for the d(Se) contribution. Contrary to SeH_6 (O_h), $\Delta\varepsilon^{-1}$ for the former (1/0.708 = 1.41) is 1.60 times larger than that in the latter (1/1.14 = 0.88). The results demonstrate that the fluorine substitution in SeF_6 (O_h) increases

Table 4. Reciprocal orbital energy differences ($\Delta\varepsilon^{-1}$) and the relative values ($\Delta\varepsilon^{-1}{}_{\rm rel}$) for the typical transitions contributing from p(Se) and d(Se) to σ^p(Se) in SeH_6 (O_h), SeF_6 (O_h), SeH_4 (TBP), and H_2SeF_2 (TBP).[a,b]

Species	$\psi_i \rightarrow \psi_a$[c]	$\sigma^p_{i\rightarrow a}$(Se)[d]	Degeneracy	p(Se)/d(Se)	$\Delta\varepsilon^{-1}$[e]	$\Delta\varepsilon^{-1}{}_{\rm rel}$
SeH_6 (O_h)	$\psi_{18}\rightarrow\psi_{29}$	−183.4	6	p(Se)	1.71	1.00
SeH_6 (O_h)	$\psi_{19}\rightarrow\psi_{26}$	−167.1[f]	1	d(Se)	2.94	1.72
SeF_6 (O_h)	$\psi_{28}\rightarrow\psi_{51}$	−380.2	6	p(Se)	1.41	0.82
SeF_6 (O_h)	$\psi_{35}\rightarrow\psi_{87}$	−138.1[g]	1	d(Se)	0.88	0.52
SeH_4 (TBP)	$\psi_{18}\rightarrow\psi_{21}$	−673.3	1	p(Se)	2.75	1.00
SeH_4 (TBP)	$\psi_{19}\rightarrow\psi_{26}$	−209.2	1	d(Se)	3.56	1.29
H_2SeF_2 (TBP)	$\psi_{22}\rightarrow\psi_{30}$	−694.5	1	p(Se)	2.28	0.83
H_2SeF_2 (TBP)	$\psi_{27}\rightarrow\psi_{30}$	−609.4	1	d(Se)[h]	3.32	1.21

[a] Calculated with the DFT-GIAO method with the 6-311+G(3df,3pd) basis sets. [b] A utility program (NMRANAL-NH03G) being employed. [c] Transition. [d] In ppm. [e] In au^{-1}. [f] The contribution from the $\psi_{20}\rightarrow\psi_{28}$ transition being −154.9 ppm, where $\varepsilon_{26}=\varepsilon_{27}=\varepsilon_{28}$. [g] The contribution from the $\psi_{34}\rightarrow\psi_{88}$ transition being −131.1 ppm, where $\varepsilon_{86}=\varepsilon_{87}=\varepsilon_{88}$. [h] The contribution from p(Se) is also large.

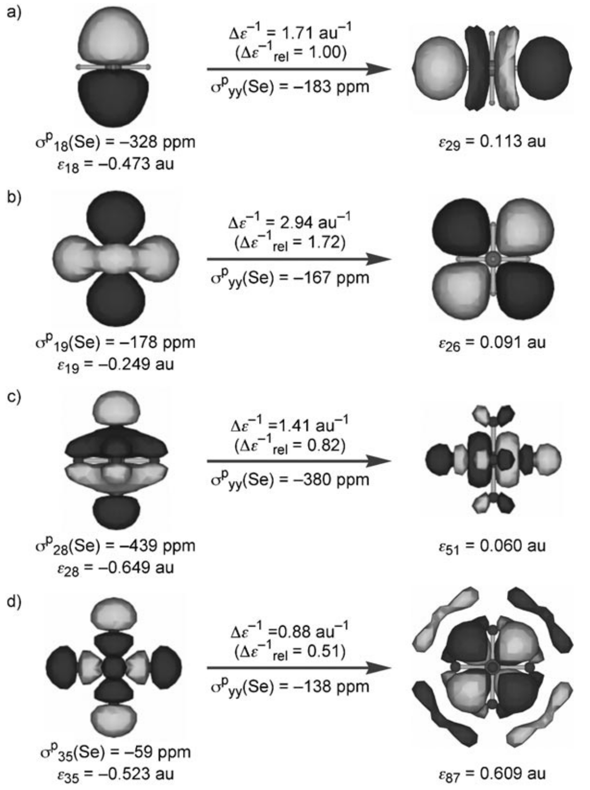

Figure 3. Main transitions in SeH_6 (O_h) and SeF_6 (O_h): a) Arising from p(Se) in SeH_6 (O_h): ψ_{16}-ψ_{18} being degenerated and ψ_{29}–ψ_{31} also degenerated, b) from d(Se) in SeH_6 (O_h): ψ_{19} and ψ_{20} being degenerated and ψ_{26}-ψ_{28} also degenerated, c) from p(Se) in SeF_6 (O_h): ψ_{28}-ψ_{30} being degenerated and ψ_{50}–ψ_{52} also degenerated, and (d) from d(Se) in SeF_6 (O_h): ψ_{34} and ψ_{35} being degenerated and ψ_{86}-ψ_{88} also degenerated. Some MOs are drawn from different directions for convenience of understanding.

$\Delta\varepsilon^{-1}{}_{\rm rel}$ for the p(Se) contribution but decreases that for the d(Se) contribution. The results are summarized in Table 4. The results give a good explanation how the fluorine substitution in SeF_6 (O_h) increases the p(Se) contributions to σ^p(Se). Indeed, there are many other transitions, but they are less important than those discussed herein.

Similar treatment is carried out in the case of SeH_4 (TBP) and H_2SeF_2 (TBP). The results are summarized in Table 4. However, the $\Delta\varepsilon^{-1}$ or $\Delta\varepsilon^{-1}{}_{\rm rel}$ values do not explain the effect. Other factor(s) must be important. Natural bond orbital (NBO) analysis[33,34] is carried out for SeH_4 (TBP) and H_2SeF_2 (TBP), together with SeH_6 (O_h) and SeF_6 (O_h), to clarify the nature of the Se−F and Se−H bonds.

Equation (2) shows the MO description of the Se−X (X = H and F) bonds estimated by the NBO analysis. Table 5 collects the coefficients (c(Se) and c(X)) and the hybrid states at Se, H, and F for the bonds in SeH_4 (TBP), H_2SeF_2 (TBP), SeH_6 (O_h), and SeF_6 (O_h). χ(Se: $s^1p^pd^df^f$) stands for the atomic orbitals of Se and χ(X: $s^1p^pd^df^f$) for those of H and F at the hybrid states ($f=0$ for H). The hybrid states are described by the p, d, and f values in Equation (2), assuming $s=1$ (see Table 5). The contributions from χ(Se) and χ(X) to $\psi_{\rm NBO}$(Se−X) are given by c^2(Se) and c^2(X), respectively, where $c^2({\rm Se}) + c^2({\rm X}) = 1.00$ in the treatment.

$$\psi_{\rm NBO}({\rm Se{-}X}) = c({\rm Se})\chi({\rm Se:\ s^1p^pd^df^f}) + c({\rm X})\chi({\rm X:\ s^1p^pd^df^f}) \tag{2}$$

The hybrid state at Se of Se−H_{eq} in H_2SeF_2 (TBP) ($p=6.08$ and $d=0.63$) is close to that of Se−H_{eq} in SeH_4 (TBP) ($p=5.05$ and $d=0.52$). However, the state at Se of Se−F_{ax} in H_2SeF_2 (TBP) ($p=4.63$ and $d=2.51$) is very different from that of Se−H_{ax} in SeH_4 (TBP) ($p=9.38$ and $d=5.12$). The p and d values for Se of Se−F_{ax} in H_2SeF_2 (TBP) decrease relative to those in SeH_4 (TBP). This should result in the decrease of the d(Se) contribution to σ^p(Se) in H_2SeF_2 (TBP) relative to the case of SeH_4 (TBP), since the p and d values for Se of Se−H_{eq} in H_2SeF_2 (TBP) remain unchanged.[35] The c^2(Se) values also support the discussion. While $c^2({\rm Se}) = 0.528$–0.544 for Se−H_{eq} in both SeH_4 (TBP) and H_2SeF_2 (TBP), $c^2({\rm Se}) = 0.135$ for Se−F_{ax} in H_2SeF_2 (TBP), which is much smaller than that for Se−H_{ax} in SeH_4 (TBP) (0.324). The Se−F_{ax} bonds in H_2SeF_2 (TBP) are substantially constructed by ψ_{19}, which is contributed from 4d(Se). The results demonstrate that the d(Se) contribution to σ^p(Se) in H_2SeF_2 (TBP) decrease relative to the case of SeH_4 (TBP) in total.[36]

Table 5 contains the results of the NBO analysis for SeF_6 (O_h) and SeH_6 (O_h). The hybrid state at Se of Se−F in SeF_6 (O_h) ($p=2.99$ and $d=2.00$) is very close to that at Se of Se−H in ($p=3.00$ and $d=2.00$). The results would not change the relative contributions from p(Se) and d(Se) to σ^p(Se) by this mechanism, since both compounds have only one type of bond.

The main reason for the decreased d(Se) contribution to σ^p(Se) in H_2SeF_2 (TBP)/SeH_4 (TBP) is demonstrated to be the lesser contribution of d(Se) to the hybrid state at Se in

Table 5. Results of NBO analysis for the Se–X (X = H and F) bonds in SeH_4 (TBP), H_2SeF_2 (TBP), SeH_6 (O_h), and SeF_6 (O_h).[a]

Species	Bond	*c*(Se)	p;d;f at Se[b]	*c*(X)	p;d;f at X[b]
SeH_4 (TBP)	Se–H_{eq}	0.7376[c]	5.05;0.52;0.00	0.6752	0.00;0.00;0.00
	Se–H_{ax}	0.5694[d]	9.38;5.12;0.09	0.8221	0.00;0.00;0.00
H_2SeF_2 (TBP)	Se–H_{eq}	0.7268[e]	6.08;0.63;0.03	0.6868	0.00;0.00;0.00
	Se–F_{ax}	0.3677[f]	4.63;2.15;0.07	0.9299	6.43;0.01;0.00
SeH_6 (O_h)	Se–H	0.6577[g]	3.00;2.00;0.00	0.7532	0.00;0.00;0.00
SeF_6 (O_h)	Se–F	0.4274[h]	2.99;2.00;0.01	0.9040	6.52;0.02;0.00

[a] Evaluated employing the 6-311+G(3df,3pd) basis sets, see Equation (2) for the definitions. [b] $s = 1.00$. [c] $c^2(\text{Se}) = 0.5441$. [d] $c^2(\text{Se}) = 0.3242$. [e] $c^2(\text{Se}) = 0.5282$. [f] $c^2(\text{Se}) = 0.1352$. [g] $c^2(\text{Se}) = 0.4326$. [h] $c^2(\text{Se}) = 0.1827$.

Se–F_{ax} relative to that in Se–H_{ax}. The increased p(Se) contributions to σ^{p}(Se) in SeF_6 (O_h)/SeH_6 (O_h) is determined to be the decreased $\Delta\varepsilon^{-1}$ (or $\Delta\varepsilon^{-1}{}_{\text{rel}}$) values for d(Se) in the main transitions.

After clarification of the contributions from p(Se) to σ^{p}(Se), the behavior of the vacant MOs is examined next.

Behavior of 4p(Se) in vacant MOs: The question to be addressed is how the energies of vacant orbitals are determined in the selenium compounds? Figures 4 and 5 show some MOs of SeH_2 (C_{2v}) and SeH^- ($C_{\infty v}$), respectively.

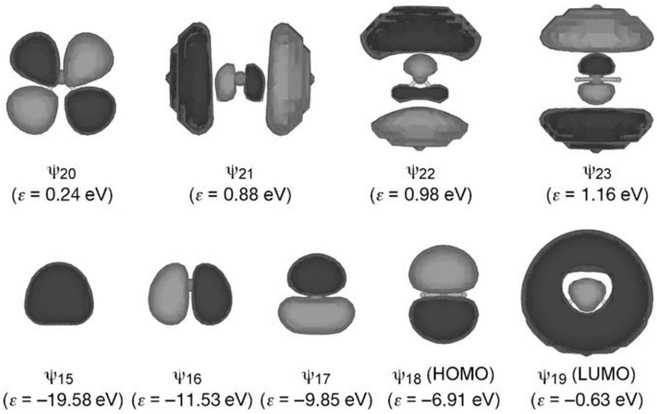

Figure 4. ψ_{15} (HOMO−3) to ψ_{23} (LUMO+4) in SeH_2 (C_{2v}), together with the energies: ψ_{18} and ψ_{23} are drawn from another direction.

SeH_2 (C_{2v}) supplies six valence AOs of 4s(Se), $4p_x$(Se), $4p_y$(Se), $4p_z$(Se), 1s(H), and 1s(H) with eight electrons. Consequently, four valence MOs are occupied and two valence MOs must be vacant. As shown in Figure 4, ψ_{15}–ψ_{18} correspond to the occupied valence MOs of σ [SeH_2: 4s(Se)], σ [SeH_2 b_2: $4p_y$(Se)], σ [SeH_2 a_1: $4p_x$(Se)], and n_p(Se) [$4p_z$(Se); HOMO], respectively: ψ_1–ψ_{14} are inner MOs. How are the vacant orbitals in SeH_2 constructed? ψ_{19} (LUMO) and ψ_{20} (LUMO+1) correspond to σ* [SeH_2 a_1: $4p_x$(Se)] and σ* [SeH_2 b_2: $4p_y$(Se)], respectively. The 5s(Se) and 4d(Se) characters contribute to ψ_{19} to some extent whereas such contributions are very low in ψ_{20}. ψ_{21}–ψ_{23} are mainly constructed by p(Se) of higher energies. There must be many vacant MOs depending on the basis sets employed in the calculations, other than ψ_{19}–ψ_{23}. They must originate from the higher state AOs of Se and H.

In the case of SeH^- ($C_{\infty v}$), five valence AOs are supplied, that is, 4s(Se), $4p_x$(Se), $4p_y$(Se), $4p_z$(Se), and 1s(H) with eight electrons. Therefore, four valence MOs are occupied whereas one must be vacant. As shown in Figure 5, ψ_{15} and ψ_{16} correspond to σ [Se–H: 4s(Se)] and σ [Se–H: $4p_x$(Se)]. ψ_{17} of n_p(Se) [$4p_y$(Se)] and ψ_{18} of n_p(Se) [$4p_z$(Se)] are degenerate with each other and they are both HOMO. ψ_1–ψ_{14} are inner MOs. The energies of the vacant orbitals in SeH^- are somewhat complex. The character of ψ_{19} (LUMO) is σ* [Se–H: 4s(Se)] with some contributions from the 4d(Se) and 5s(Se) characters (cf: ψ_{19} of SeH_2). Indeed, ψ_{20} is σ* [Se–H: p_x(Se)], but it is constructed by the higher state of p_x(Se) (cf: ψ_{21} and ψ_{22} in SeH_2). Similarly, the characters of ψ_{21} and ψ_{22} are p_y(Se) and p_z(Se), respectively, but they are constructed by the higher states of p_y(Se) and p_z(Se), respectively (cf: ψ_{23} in SeH_2). ψ_{23} (LUMO+4) is assigned to σ* [Se–H: $4p_x$(Se)] (cf: ψ_{20} in SeH_2). We must be careful when vacant orbitals are discussed, since the energy sequence is not always that expected from the AO energies.

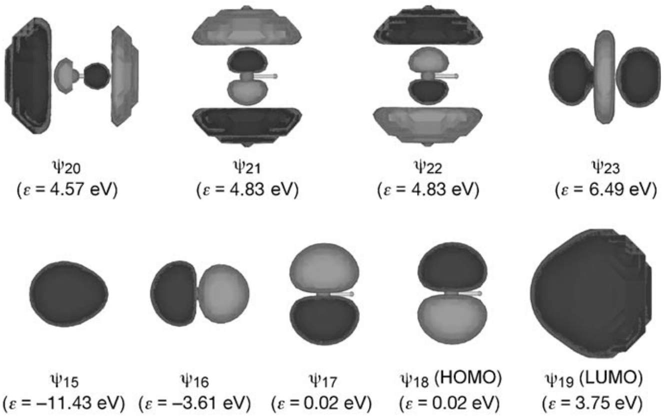

Figure 5. ψ_{15} (HOMO−3) to ψ_{23} (LUMO+4) in SeH^- ($C_{\infty v}$), together with the energies: ψ_{18} and ψ_{21} are drawn from another direction.

We must further be careful when the behavior of 4p(Se) in vacant orbitals are discussed. The inner AOs, valence AOs, and AOs of higher energy states are constructed by a set of Gaussian functions, which are commonly used to construct the AOs in the Gaussian program. Therefore, it is difficult to separate the valence AOs completely from AOs of higher energy states. The evaluation of the 4p(Se) contributions would be more difficult as the compounds become more complex due to the high complexity of MOs. However, it is strongly suggested that p(Se) of higher energy levels would not contribute to σ^{p}(Se) as much whereas 4p(Se) should contribute substantially for usual selenium compounds.[37]

How do 4p(Se) in vacant MOs contribute to σ^p(Se)? The contributions of the transitions from the occupied valence MOs to the unoccupied valence MOs are examined next. The evaluated values must correspond to the contributions from the valence 4p(Se) AOs.[38] The contributions of the transitions from occupied MOs of $\psi_{15}-\psi_{18}$ to vacant MOs of ψ_{19}, ψ_{20}, and ψ_{24} are added for SeH_2 (C_{2v}) and those from $\psi_i=\psi_{15}-\psi_{18}$ to $\psi_a=\psi_{23}$ transitions are added for SeH^- ($C_{\infty v}$),[39] for example. Table 6 shows the results for SeH_2 (C_{2v}) and SeH^- ($C_{\infty v}$), together with SeH_3^+ (C_{3v}) and SeH_4 (T_d) which have been evaluated similarly. The evaluated 4p(Se) contributions to σ^p(Se) are around 90% or larger for the compounds. The large 4p(Se) contribution strongly suggests that 4p(Se) in vacant orbitals mainly controls σ^p(Se) of usual selenium compounds.

Table 6. Contributions from atomic 4p(Se) orbitals to σ^p(Se) in some selenium compounds.[a,b]

Species	i in ψ_i	a in ψ_a	4p(Se)[c]	σ^p(Se)[c]	% 4p(Se)
SeH^- ($C_{\infty v}$)	15–18	23	−481.2	−501.5	96.0
SeH_2 (C_{2v})	15–18	19, 20, 24	−866.2	−928.8	93.3
SeH_3^+ (C_{3v})	15–18	19–21	−947.1	−1079.9	87.7
SeH_4 (T_d)	15–18	20–22	−1528.2	−1666.8	91.7

[a] Calculated with the DFT-GIAO method employing the 6-311+G-(3df,3pd) basis sets. [b] A utility program (NMRANAL-NH03G) being employed. [c] In ppm.

Conclusions

Atomic 4p(Se) orbitals are expected predominantly to determine δ(Se), however, 4d(Se) must also play an important role when the Se atoms are highly coordinated. It is necessary to clarify the contributions from p(Se) and d(Se) to σ^p(Se) in various selenium compounds to establish standard rules that are useful to determine geometric and electronic structures based on δ(Se). Contributions from p(Se) and d(Se) to σ^p(Se) are evaluated for Se^*H_n (* = null, +, or −) and some oxides to build the image for the contributions. Effects of methyl and halogen substitutions are also examined.

The p(Se) contributions are higher than 96% for SeH^- ($C_{\infty v}$), SeH_2 (C_{2v}), SeH_3^+ (C_{3v}), SeH_3^+ (D_{3h}), and SeH_4 (T_d). The contributions are 75–80% for SeH_4 (TBP), SeH_5^+ (TBP), SeH_5^+ (SP), and SeH_5^- (SP) and 79–92% for H_2SeO (C_s), H_4SeO (C_{2v}), and H_2SeO_2 (C_{2v}). The Me and X substitutions increase the p(Se) contributions by 1–2 (per Me) and 4–6% (per X). Therefore, σ^p(Se) of usual selenium compounds can be analyzed based on p(Se). In the case of SeH_6 (O_h), the p(Se) contribution is 52%. However, the contribution is also increased to about 85% in $HSeF_5$, $MeSeF_5$, and SeF_6 by the Me and X substitutions. Consequently, the σ^p(Se) values of these compounds can also be analyzed mainly based on p(Se) with some corrections by d(Se). The contributions from f(Se) are negligible and those from AOs at other nuclei are small. The results will help to establish a new method to analyze the chemical shifts separately by the factors, which contribute to the chemical shifts.

Acknowledgements

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[11] The total absolute magnetic shielding tensors (σ^t) are decomposed into diamagnetic (σ^d) and paramagnetic (σ^p) contributions ($\sigma^t=\sigma^d+\sigma^p$). This decomposition includes small arbitrariness due to the coordinate origin dependence. However, it does not diminish our chemical analyses and insights into the ^{77}Se NMR spectroscopy.

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[13] The observed δ(Se) values of various selenium compounds are well explained by the σ^{t}(Se) values calculated with the DFT-GIAO method employing the 6-311++G(3df,2pd) basis sets at the non-relativistic level. The correlation between the two is as follows, where the relative values from MeSeMe are employed for the plot (ex: $\sigma^{t}(\mathrm{Se}{:}\ \boldsymbol{M})_{\mathrm{calcd:rel}} = -(\sigma^{t}(\mathrm{Se}{:}\ \boldsymbol{M})_{\mathrm{calcd}} - \sigma^{t}(\mathrm{Se}{:}\ \mathrm{MeSeMe})_{\mathrm{calcd}})$): $\delta(\mathrm{Se}{:}\ \boldsymbol{M})_{\mathrm{obsd:rel}} = 0.981\times\sigma^{t}(\mathrm{Se}{:}\ \boldsymbol{M})_{\mathrm{calcd:rel}} + 24.3$ ($r=0.998$) The correlation is very good with the *a* and *r* values being very close to 1.00 with the small b value if one consider the chemical shift range of over 1500 ppm and the solvent effect on the charged and/or polar selenium compounds. The relativistic effect seems to change not so severely compound to compound although the relativistic terms may contribute to some extent; see ref. [8c].

[14] σ^{p} and σ^{d} are exactly expressed by the Ramsey's Equation.[15] They are approximately calculated in the framework of the Hartree–Fock (H-F) or DFT theory.[16]

[15] N. F. Ramsey, *Phys. Rev.* **1950**, *77*, 567; N. F. Ramsey, *Phys. Rev.* **1950**, *78*, 699–703; N. F. Ramsey, *Phys. Rev.* **1951**, *83*, 540–541; N. F. Ramsey, E. M. Purcell, *Phys. Rev.* **1952**, *85*, 143–144; N. F. Ramsey, *Phys. Rev.* **1953**, *91*, 303–307; N. F. Ramsey, *Phys. Rev.* **1952**, *86*, 243–246.

[16] Based on the second-order perturbation theory at the level of the H-F and single-excitation CI approximation, $\sigma^{p}_{i\to j}$ on a resonance nucleus *N* is shown to be proportional to reciprocal orbital energy gap $(\varepsilon_j - \varepsilon_i)^{-1}$, and approximately expressed in Equation (1), where ψ_k is the *k*-th orbital function, $\hat{L}_{z,N}$ is orbital angular momentum around the resonance nucleus, and r_{N} is the distance from the nucleus *N*. See also refs. [8,9,14].

[17] W. Nakanishi, S. Hayashi, D. Yamaki, M. Hada, *Chem. Eur. J.* **2008**, *14*, 7278–7284. The charges at Se (Q(Se)) are calculated at the NBO level, if necessary.[33,34]

[18] The $\langle r_{\mathrm{Se}}^{-3}\rangle_{4p}$ values for both HOMO and LUMO constructed by pure atomic 4p(Se) orbitals are well correlated with the charges at Se (Q(Se)). The correlation calculated for Se^{4+}, Se^{2+}, Se^{0}, and Se^{2-} with the B3LYP/6-311+G(3df) method is as follows: $y=2.545\exp(0.0637x)-1.545$ ($R^2=1.000$), where $(x,y)=(\langle r_{\mathrm{Se}}^{-3}\rangle_{4p}, Q(\mathrm{Se}))$.

[19] No contributions are from atomic s orbitals to σ^{p}(Se).

[20] For the 6-311G(3d) basis sets see, a) R. C. Binning, Jr., L. A. Curtiss, *J. Comput. Chem.* **1990**, *11*, 1206–1216; b) L. A. Curtiss, M. P. McGrath, J.-P. Blaudeau, N. E. Davis, R. C. Binning, Jr., L. Radom, *J. Chem. Phys.* **1995**, *103*, 6104–6113; c) M. P. McGrath, L. Radom, *J. Chem. Phys.* **1991**, *94*, 511–516. For the diffuse functions (+ and ++) see, T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. von R. Schleyer, *J. Comput. Chem.* **1983**, *4*, 294–301.

[21] The 6-311+G(3df,3pd) basis sets are contained in the 6-311G(3d) basis sets system.[18]

[22] Gaussian 03, Revision D.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

[23] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100; A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789; B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200–206.

[24] K. Wolinski, J. F. Hinton, P. Pulay, *J. Am. Chem. Soc.* **1990**, *112*,8251–8260; K. Wolinski, A. Sadlej, *Mol. Phys.* **1980**, *41*, 1419–1430; R. Ditchfield, *Mol. Phys.* **1974**, *27*, 789–807; R. McWeeny, *Phys. Rev.* **1962**, *126*, 1028–1034; F. London, *J. Phys. Radium, Paris* **1937**, *8*, 397–409.

[25] Occupied MOs are denoted by ψ_i, ψ_j,…; unoccupied MOs by ψ_a, ψ_b,… unless otherwise noted. The $\psi_i\to\psi_j$ transition should be described as $\psi_i\to\psi_j$ ($j \neq i$). However, we write it as $\psi_i\to\psi_j$, since the contribution from the $\psi_i\to\psi_i$ transition is intrinsically zero.

[26] The σ^{p}(Se) values contributed from the Occ-to-Occ transitions are about 200–400 ppm in Se*H_n. The values shift downfield (ca. 100 to −200 ppm) by the methyl and halogen substitutions in R_rSe*X_xO_o (*=null, +, or −).

[27] The contribution from the $\psi_i\to\psi_j$ (Occ-to-Occ) transitions ($\sigma^{p}_{i\to j}$(Se)) in a selenium compound can be fractionalized to each MO. There must be various methods for the fractionalization. The contribution from a $\psi_i\to\psi_j$ transition ($\sigma^{p}_{i\to j}$(Se)) cannot be differentiated from that of the $\psi_j\to\psi_i$ transition ($\sigma^{p}_{j\to i}$(Se)), as approximately expressed by Equation (1). Therefore, it would be reasonable that $\sigma^{p}_{i\to j}$(Se)/2 belongs to ψ_i and $\sigma^{p}_{i\to j}$(Se)/2 to ψ_j. This method is employed in our treatment. In this treatment, rather large negative values are assigned to inner MOs, constructed by atomic 3p(Se) orbitals. Contributions from 3d(Se) are not negligible, either. The results may come from the energy differences, which are substantially zero due to the degeneracy or close to degeneracy in 3d(Se).

[28] Table S1 of the Supporting Information collects the results of the fractionalized σ^{p}_{i} for ψ_i in Se*H_n (*=null, +, or −) by the method.[26]

[29] The σ^{p}(Se) values contributed from the $\psi_i\to\psi_j$ (Occ-to-Occ) transitions must be discussed for some cases such as the β-effect in RSeR′.[10]

[30] The lone pair orbital in $\mathrm{SeH_5^-}$ (C_{4v}; SP) (ψ_{20}) could be assigned mainly to the Se−H bonds of the basal positions. In this case, n_{lp} would be 0. See ψ_{20} of $\mathrm{SeH_5^-}$ in Figure 1.

[31] The methyl substitution on $\mathrm{SeH_3^+}$ (D_{3h}) exceptionally decreases the p(Se) contributions, although the magnitude is very small (0.5 % per Me).

[32] It is worthwhile to note that the contribution from χ(Me) amounts to 131 ppm for $\mathrm{SeMe_6}$ (C_i) (22 ppm per Me). The value is much larger than the usual cases such as $\mathrm{SeMe_2}$ (C_{2v}) (5 ppm per Me). The contributions in $\mathrm{SeMe_5^+}$ (SP) and $\mathrm{SeMe_5^-}$ (SP) are also large (91–97 ppm).

[33] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735–746; J. E. Carpenter, F. Weinhold, *J. Mol. Struct. (THEOCHEM)* **1988**, *169*, 41–62.

[34] NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, **2001**.

[35] The (*s,p,d,f*) values for the hybrid state at ns(Se) in $\mathrm{H_4Se}$ (TBP) and $\mathrm{H_2SeF_2}$ (TBP) are (1.00,0.59,0.00,0.00) and (1.00,0.44,0.00,0.00), respectively. Therefore, the hybrid states in $\mathrm{H_4Se}$ (TBP) and $\mathrm{H_2SeF_2}$ (TBP) are unchanged.

[36] The results of NBO analysis must be carefully examined when σ^{p}_{i}(Se) are discussed based on the results, since σ^{p}_{i}(Se) usually changes depending on each ψ_i. However, σ^{p}_{i}(Se) for ψ_{16}–ψ_{18} in $\mathrm{SeH_4}$ (TBP) are not so different, which are −316 to −448 ppm as shown in Table 1.

[37] The expectation comes from the behavior of $\langle r^{-3}\rangle$, which is discussed in Table S2 of the Supporting Information.

[38] If a occupied valence orbital (ψ_i) is consisted with 4s(Se) and 4p(Se) and if a vacant orbital (ψ_a) contains the 4p(Se) and 4d(Se) characters, the $\psi_i \rightarrow \psi_a$ transition will evaluate the contribution only from 4p(Se), since the transition from p(Se) to d(Se) vanishes due to the symmetry requirement and the contribution from s(Se) must be null.

[39] Such treatment would evaluate the lower limit of the contributions from 4p(Se) to σ^p(Se), since the 4p(Se) character would spread over other orbitals.

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