

Table 2.12 – continued from previous page

| Basis Set           | Elem. | ECP | Comment |
|---------------------|-------|-----|---------|
| 6-31++G**           | H-Zn  | –   |         |
| 6-31++G (d, p)      | H-Zn  | –   |         |
| 6-31++G (2d, p)     | H-Zn  | –   |         |
| 6-31++G (2d, 2p)    | H-Zn  | –   |         |
| 6-31++G (2df, 2p)   | H-Zn  | –   |         |
| 6-31++G (2df, 2pd)  | H-Zn  | –   |         |
| 6-311G              | H-Br  | –   |         |
| 6-311G*             | H-Br  | –   |         |
| 6-311G**            | H-Br  | –   |         |
| 6-311G (d)          | H-Br  | –   |         |
| 6-311G (d, p)       | H-Br  | –   |         |
| 6-311G (2d)         | H-Br  | –   |         |
| 6-311G (2d, p)      | H-Br  | –   |         |
| 6-311G (2d, 2p)     | H-Br  | –   |         |
| 6-311G (2df)        | H-Br  | –   |         |
| 6-311G (2df, 2p)    | H-Br  | –   |         |
| 6-311G (2df, 2pd)   | H-Br  | –   |         |
| 6-311G (3df)        | H-Br  | –   |         |
| 6-311G (3df, 3pd)   | H-Br  | –   |         |
| 6-311+G*            | H-Br  | –   |         |
| 6-311+G**           | H-Br  | –   |         |
| 6-311+G (d)         | H-Br  | –   |         |
| 6-311+G (d, p)      | H-Br  | –   |         |
| 6-311+G (2d)        | H-Br  | –   |         |
| 6-311+G (2d, p)     | H-Br  | –   |         |
| 6-311+G (2d, 2p)    | H-Br  | –   |         |
| 6-311+G (2df)       | H-Br  | –   |         |
| 6-311+G (2df, 2p)   | H-Br  | –   |         |
| 6-311+G (2df, 2pd)  | H-Br  | –   |         |
| 6-311+G (3df)       | H-Br  | –   |         |
| 6-311+G (3df, 2p)   | H-Br  | –   |         |
| 6-311+G (3df, 3pd)  | H-Br  | –   |         |
| 6-311++G**          | H-Br  | –   |         |
| 6-311++G (d, p)     | H-Br  | –   |         |
| 6-311++G (2d, p)    | H-Br  | –   |         |
| 6-311++G (2d, 2p)   | H-Br  | –   |         |
| 6-311++G (2df, 2p)  | H-Br  | –   |         |
| 6-311++G (2df, 2pd) | H-Br  | –   |         |
| 6-311++G (3df, 3pd) | H-Br  | –   |         |

## Ahlrichs Basis Sets

The older Ahlrichs basis sets implemented in ORCA cover all-electron basis sets and the basis sets automatically employing the def-ECP for all elements beyond Rb. A list of available Ahlrichs basis sets is given in [Table 2.13](#). Relativistically recontracted variants are shown in [Section 2.7.3](#).

### Note

Past versions of ORCA (ORCA <4.0) used to load all-electron basis sets also for elements Rb-I with the below keywords for double- and triple- $\zeta$  basis sets. The Rb-I basis sets originated from non-relativistic all-electron basis sets of the Turbomole library (such as “TZVPAlls”). **This automatic substitution is now deprecated.** However, we offer temporarily the ability to reproduce that behavior by adding the prefix “old-” to the below keywords, e.g. old-TZVP.

Table 2.13: Available all-electron Ahlrichs basis sets.

| Basis Set   | Elem. | ECP             | Comment   |
|---|-------|-----------------|---|
| SV  | H–Kr  | –               | Valence double-zeta basis set.                                |
| SV (P)  | H–Kr  | –               | Valence double-zeta with polarization only on heavy elements. |
| SVP   | H–Kr  | –               | Polarized valence double-zeta basis set.                      |
| TZV   | H–Kr  | –               | Valence triple-zeta basis set.                                |
| TZV (P)   | H–Kr  | –               | Valence triple-zeta with polarization on heavy elements.      |
| TZVP  | H–Kr  | –               | Polarized valence triple-zeta basis set.                      |
| TZVPP   | H–Kr  | –               | Doubly polarized triple-zeta basis set.                       |
| QZVP  | H–Kr  | –               | Polarized valence quadruple-zeta basis set.                   |
| QZVPP   | H–Kr  | –               | Doubly polarized quadruple-zeta basis set.                    |
| def–SV (P)  | H–Lr  | def–ECP (Rb–Lr) | Valence double-zeta with polarization only on heavy elements. |
| def–SVP   | H–Lr  | def–ECP (Rb–Lr) | Polarized valence double-zeta basis set.                      |
| def–TZVP  | H–Lr  | def–ECP (Rb–Lr) | Valence triple-zeta basis set with polarization functions.    |
| def–TZVPP   | H–Lr  | def–ECP (Rb–Lr) | Doubly polarized triple-zeta basis set.                       |
| <i>Minimally augmented</i> (scheme by Truhlar et al.[17]) |       |                 |   |
| ma–def–TZVP   | Fr–Lr | def–ECP (Fr–Lr) | Minimally augmented def–TZVP basis set.                       |
| <i>Legacy definitions (not recommended!)</i>              |       |                 |   |
| old–SV  | H–I   | –               |   |
| old–SV (P)  | H–I   | –               |   |
| old–SVP   | H–I   | –               |   |
| old–TZV   | H–I   | –               |   |
| old–TZV (P)   | H–I   | –               |   |
| old–TZVP  | H–I   | –               |   |
| old–TZVPP   | H–I   | –               |   |

## Karlsruhe def2 Basis Sets

The valence polarized basis sets of the Karlsruhe def2 family are all-electron for elements **H–Kr**, and automatically load Stuttgart-Dresden *effective core potentials* for elements **Rb–Rn**. A list of available Karlsruhe def2 basis sets is given in Table 2.14. Relativistically recontracted variants are discussed in Section 2.7.3.

Table 2.14: Available Karlsruhe def2 basis sets.

| Basis Set   | Elem. | ECP              | Comment  |
|---|-------|------------------|--|
| def2–SVP  | H–Rn  | def2–ECP (Rb–Rn) | Polarized valence double- $\zeta$ .  |
| def2–SV (P)   | H–Rn  | def2–ECP (Rb–Rn) | def2–SVP with slightly reduced polarization.   |
| def2–TZVP   | H–Rn  | def2–ECP (Rb–Rn) | Polarized valence triple- $\zeta$ . Quite similar to the older def–TZVPP for main group elements and TZVP for H. |
| def2–TZVP (–f)  | H–Rn  | def2–ECP (Rb–Rn) | def2–TZVP with f polarization removed from main group elements.  |
| def2–TZVPP  | H–Rn  | def2–ECP (Rb–Rn) | Doubly polarized valence triple- $\zeta$ .   |
| def2–QZVP   | H–Rn  | def2–ECP (Rb–Rn) | Polarized valence quadruple- $\zeta$ .   |
| def2–QZVPP  | H–Rn  | def2–ECP (Rb–Rn) | Doubly polarized valence quadruple- $\zeta$ .  |
| <i>Diffuse</i> (Rappoport et al.[18, 19])                 |       |                  |  |
| def2–SVPD   | H–Rn  | def2–ECP (Rb–Rn) | Diffuse def2–SVP basis set for property calculations   |
| def2–TZVPD  | H–Rn  | def2–ECP (Rb–Rn) | Diffuse def2–TZVP basis set for property calculations  |
| def2–TZVPPD   | H–Rn  | def2–ECP (Rb–Rn) | Diffuse def2–TZVPP basis set for property calculations   |
| def2–QZVPD  | H–Rn  | def2–ECP (Rb–Rn) | Diffuse def2–QZVP basis set for property calculations  |
| def2–QZVPPD   | H–Rn  | def2–ECP (Rb–Rn) | Diffuse def2–QZVPP basis set for property calculations   |
| <i>Minimally augmented</i> (scheme by Truhlar et al.[17]) |       |                  |  |
| ma–def2–SVP   | H–Rn  | def2–ECP (Rb–Rn) | Minimally augmented def2–SVP basis set.  |
| ma–def2–SV (P)  | H–Rn  | def2–ECP (Rb–Rn) | Minimally augmented def2–SV(P) basis set.  |
| ma–def2–mSVP  | H–Rn  | def2–ECP (Rb–Rn) | Minimally augmented def2–mSVP basis set.   |
| ma–def2–TZVP  | H–Rn  | def2–ECP (Rb–Rn) | Minimally augmented def2–TZVP basis set.   |
| ma–def2–TZVP (–f)   | H–Rn  | def2–ECP (Rb–Rn) | Minimally augmented def2–TZVP(–f) basis set.   |
| ma–def2–TZVPP   | H–Rn  | def2–ECP (Rb–Rn) | Minimally augmented def2–TZVPP basis set.  |
| ma–def2–QZVPP   | H–Rn  | def2–ECP (Rb–Rn) | Minimally augmented def2–QZVPP basis set.  |

## Karlsruhe dhf Basis Sets

These basis sets are derived from the def2-XVP ones with small modifications for 5s, 6s, 4d, and 5d elements and iodine.[20] They are optimized for the revised Dirac-Fock ECPs (dhf-ECP) as opposed to the Wood-Boring ones (def2-ECP). For elements H–Kr these basis sets are equivalent to the respective *def2-XVP* basis set. Versions for two-component methods are also available, e.g. dhf-TZVP-2c, **however, such methods are currently not implemented in ORCA**. A list of available Karlsruhe dhf basis sets is given in Table 2.15.

Table 2.15: Available dhf basis sets.

| Basis Set                      | Elem. | ECP                | Comment             |
|--------------------------------|-------|--------------------|---------------------|
| dhf-SV(P)                      | H–Rn  | dhf-ECP (Rb–Rn)    | based on def2-SV(P) |
| dhf-SVP                        | H–Rn  | dhf-ECP (Rb–Rn)    | based on def2-SVP   |
| dhf-TZVP                       | H–Rn  | dhf-ECP (Rb–Rn)    | based on def2-TZVP  |
| dhf-TZVPP                      | H–Rn  | dhf-ECP (Rb–Rn)    | based on def2-TZVPP |
| dhf-QZVP                       | H–Rn  | dhf-ECP (Rb–Rn)    | based on def2-QZVP  |
| dhf-QZVPP                      | H–Rn  | dhf-ECP (Rb–Rn)    | based on def2-QZVPP |
| <i>Two-component variants:</i> |       |                    |                     |
| dhf-SVP-2c                     | H–Rn  | dhf-ECP-2c (Rb–Rn) | based on def2-SVP   |
| dhf-TZVP-2c                    | H–Rn  | dhf-ECP-2c (Rb–Rn) | based on def2-TZVP  |
| dhf-TZVPP-2c                   | H–Rn  | dhf-ECP-2c (Rb–Rn) | based on def2-TZVPP |
| dhf-QZVP-2c                    | H–Rn  | dhf-ECP-2c (Rb–Rn) | based on def2-QZVP  |
| dhf-QZVPP-2c                   | H–Rn  | dhf-ECP-2c (Rb–Rn) | based on def2-QZVPP |

## Jensen Basis Sets

Jensen’s polarization-consistent generally contracted basis sets include various general purpose and specialized variants. A list of available Jensen basis sets is given in Table 2.16.[21, 22, 23, 24, 25, 26, 27]

Table 2.16: Available Jensen basis sets.

| Basis Set   | Elem.          | ECP | Comment                                 |
|---|----------------|-----|---|
| pc-0  | H–Ca,<br>Ga–Kr | –   |   |
| pc-1  | H–Kr           | –   |   |
| pc-2  | H–Kr           | –   |   |
| pc-3  | H–Kr           | –   |   |
| pc-4  | H–Kr           | –   |   |
| aug-pc-0  | H–Ca,<br>Ga–Kr | –   | pc-0 augmented by diffuse functions     |
| aug-pc-1  | H–Kr           | –   | pc-1 augmented by diffuse functions     |
| aug-pc-2  | H–Kr           | –   | pc-2 augmented by diffuse functions     |
| aug-pc-3  | H–Kr           | –   | pc-3 augmented by diffuse functions     |
| aug-pc-4  | H–Kr           | –   | pc-4 augmented by diffuse functions     |
| <i>Segmented contraction variants:</i>            |                |     |   |
| pcseg-0   | H–Kr           | –   |   |
| pcseg-1   | H–Kr           | –   |   |
| pcseg-2   | H–Kr           | –   |   |
| pcseg-3   | H–Kr           | –   |   |
| pcseg-4   | H–Kr           | –   |   |
| aug-pcseg-0                                       | H–Kr           | –   | pcseg-0 augmented by diffuse functions  |
| aug-pcseg-1                                       | H–Kr           | –   | pcseg-1 augmented by diffuse functions  |
| aug-pcseg-2                                       | H–Kr           | –   | pcseg-2 augmented by diffuse functions  |
| aug-pcseg-3                                       | H–Kr           | –   | pcseg-3 augmented by diffuse functions  |
| aug-pcseg-4                                       | H–Kr           | –   | pcseg-4 augmented by diffuse functions  |
| <i>Optimized for nuclear magnetic shieldings:</i> |                |     |   |
| pcSseg-0  | H–Kr           | –   |   |
| pcSseg-1  | H–Kr           | –   |   |
| pcSseg-2  | H–Kr           | –   |   |
| pcSseg-3  | H–Kr           | –   |   |
| pcSseg-4  | H–Kr           | –   |   |
| aug-pcSseg-0                                      | H–Kr           | –   | pcSseg-0 augmented by diffuse functions |
| aug-pcSseg-1                                      | H–Kr           | –   | pcSseg-1 augmented by diffuse functions |
| aug-pcSseg-2                                      | H–Kr           | –   | pcSseg-2 augmented by diffuse functions |
| aug-pcSseg-3                                      | H–Kr           | –   | pcSseg-3 augmented by diffuse functions |
| aug-pcSseg-4                                      | H–Kr           | –   | pcSseg-4 augmented by diffuse functions |

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| Basis Set  | Elem.                  | ECP | Comment                              |
|--|------------------------|-----|--------------------------------------|
| <i>Optimized for spin-spin coupling constants:</i> |                        |     |                                      |
| pcJ-0  | H-He, B-<br>Ne, Al-Ar  | –   |                                      |
| pcJ-1  | H-He, B-<br>Ne, Al-Ar  | –   |                                      |
| pcJ-2  | H-He, B-<br>Ne, Al-Ar  | –   |                                      |
| pcJ-3  | H-He, B-<br>Ne, Al-Ar  | –   |                                      |
| pcJ-4  | H-He, B-<br>Ne, Al-Ar  | –   |                                      |
| aug-pcJ-0  | H-He, B-<br>Ne, Al-Ar  | –   | pcJ-0 augmented by diffuse functions |
| aug-pcJ-1  | H-He, B-<br>Ne, Al-Ar  | –   | pcJ-1 augmented by diffuse functions |
| aug-pcJ-2  | H-He, B-<br>Ne, Al-Ar  | –   | pcJ-2 augmented by diffuse functions |
| aug-pcJ-3  | H-He, B-<br>Ne, Al-Ar  | –   | pcJ-3 augmented by diffuse functions |
| aug-pcJ-4  | H-He, B-<br>Ne, Al-Ar  | –   | pcJ-4 augmented by diffuse functions |
| <i>Optimized for hyperfine coupling constants:</i> |                        |     |                                      |
| pcH-1  | H, He, B-<br>Ne, Al-Ar | –   |                                      |
| pcH-2  | H, He, B-<br>Ne, Al-Ar | –   |                                      |
| pcH-3  | H, He, B-<br>Ne, Al-Ar | –   |                                      |
| pcH-4  | H, He, B-<br>Ne, Al-Ar | –   |                                      |
| aug-pcH-1  | H, He, B-<br>Ne, Al-Ar | –   | pcH-1 augmented by diffuse functions |
| aug-pcH-2  | H, He, B-<br>Ne, Al-Ar | –   | pcH-2 augmented by diffuse functions |
| aug-pcH-3  | H, He, B-<br>Ne, Al-Ar | –   | pcH-3 augmented by diffuse functions |
| aug-pcH-4  | H, He, B-<br>Ne, Al-Ar | –   | pcH-4 augmented by diffuse functions |
| <i>Optimized for core-spectroscopy:</i>            |                        |     |                                      |
| pcX-1  | Li-Ar                  | –   |                                      |
| pcX-2  | Li-Ar                  | –   |                                      |
| pcX-3  | Li-Ar                  | –   |                                      |
| pcX-4  | Li-Ar                  | –   |                                      |
| aug-pcX-1  | Li-Ar                  | –   | pcX-1 augmented by diffuse functions |
| aug-pcX-2  | Li-Ar                  | –   | pcX-2 augmented by diffuse functions |
| aug-pcX-3  | Li-Ar                  | –   | pcX-3 augmented by diffuse functions |
| aug-pcX-4  | Li-Ar                  | –   | pcX-4 augmented by diffuse functions |

## Hydrogenic Gaussian Basis Sets

Lehtolas hydrogenic Gaussian basis sets (HGBS) were constructed as widely transferable and accurate basis sets based on one-electron model systems imitating real atoms and molecules.[28] A list of available HGBS basis sets is given in Table 2.17.

### Naming convention of HGBS basis sets

- $m$ : represents the energy optimization threshold  $10^{-m}$
- $Pn$ : represents the number of polarization shells
- $A$ : indicates explicit augmentation by diffuse functions

Table 2.17: Karlsruhe HGBS, HGBSP, AHGBS, and AHGBSP basis sets.

| Basis Set | Elem. | ECP | Comment  |
|-----------|-------|-----|--|
| HGBS-5    | H-Og  | –   |  |
| HGBS-7    | H-Og  | –   |  |
| HGBS-9    | H-Og  | –   |  |
| HGBSP1-5  | H-Og  | –   | Polarized variant                                |
| HGBSP1-7  | H-Og  | –   |  |
| HGBSP1-9  | H-Og  | –   |  |
| HGBSP2-5  | H-Og  | –   |  |
| HGBSP2-7  | H-Og  | –   |  |
| HGBSP2-9  | H-Og  | –   |  |
| HGBSP3-5  | H-Og  | –   |  |
| HGBSP3-7  | H-Og  | –   |  |
| HGBSP3-9  | H-Og  | –   |  |
| AHGBS-5   | H-Og  | –   | Augmented by diffuse functions                   |
| AHGBS-7   | H-Og  | –   |  |
| AHGBS-9   | H-Og  | –   |  |
| AHGBSP1-5 | H-Og  | –   | Polarized variant augmented by diffuse functions |
| AHGBSP1-7 | H-Og  | –   |  |
| AHGBSP1-9 | H-Og  | –   |  |
| AHGBSP2-5 | H-Og  | –   |  |
| AHGBSP2-7 | H-Og  | –   |  |
| AHGBSP2-9 | H-Og  | –   |  |
| AHGBSP3-5 | H-Og  | –   |  |
| AHGBSP3-7 | H-Og  | –   |  |
| AHGBSP3-9 | H-Og  | –   |  |

## Sapporo Basis Sets

The Sapporo basis set family, named after the city of Sapporo, Japan, comprises segmented contracted all-electron Gaussian basis sets up to quadruple- $\zeta$  quality.[29, 30, 31] They were developed as compact yet accurate basis sets focusing on calculations with correlated wavefunction methods. Variants optimized for the scalar-relativistic DKH3 Hamiltonian are also available. A list of available Sapporo basis sets is given in Table 2.18. Relativistic variants are discussed in Section 2.7.3.

Table 2.18: List of available Sapporo basis sets.

| Basis Set        | Elem. | ECP | Comment |
|------------------|-------|-----|---------|
| Sapporo-DZP-2012 | H-Xe  | –   |         |
| Sapporo-TZP-2012 | H-Xe  | –   |         |
| Sapporo-QZP-2012 | H-Xe  | –   |         |

## Partridge Basis Sets

The basis sets of the Partridge family are uncontracted RHF groundstate energy-optimized.[32, 33] A list of available Partridge basis sets is given in Table 2.19.

Table 2.19: Available Partridge basis sets.

| Basis Set   | Elem.    | ECP | Comment |
|-------------|----------|-----|---------|
| Partridge-1 | H, Li-Sr | –   |         |
| Partridge-2 | H, Li-Kr | –   |         |
| Partridge-3 | H, Li-Zn | –   |         |
| Partridge-4 | Sc-Zn    | –   |         |

## CRENB Basis Sets

The Christiansen-Ross-Ermiler-Nash-Bursten (CRENB) basis sets and *effective core potentials* are available for most elements.[34, 35, 36, 37, 38, 39, 40] Note that while the ECPs were originally designed for spin-orbit coupling (SOC) interactions, **SOC calculations with ECPs are currently not implemented in ORCA**. A list of available CRENB basis sets is given in Table 2.20.

Table 2.20: List of available CRENB basis sets.

| Basis Set | Elem.    | ECP                | Comment  |
|-----------|----------|--------------------|--|
| CRENBL    | H, Li–Og | CRENBL–ECP (Li–Og) | Large basis version for use with <i>small-core</i> ECP |

## LANL Basis Sets

The Los Alamos National Laboratory (LANL) basis sets and *effective core potentials* were originally introduced in 1985 by Hay and Wadt.[41, 42, 43] Later polarized variants were proposed[44, 45] and the basis sets were extended by Roy et al.[46]. A list of available LANL basis sets is given in Table 2.21.

Table 2.21: List of available LANL basis sets.

| Basis Set   | Elem.                  | ECP                              | Comment                         |
|-------------|------------------------|----------------------------------|---------------------------------|
| LANL08      | Na–La, Hf–Bi           | HayWadt (Na–La, Hf–Bi)           | uncontracted                    |
| LANL08 (f)  | Sc–Cu, Y–Ag, La, Hf–Au | HayWadt (Sc–Cu, Y–Ag, La, Hf–Au) | uncontracted + polarization     |
| LANL2DZ     | H, Li–La, Hf–Bi, U–Pu  | HayWadt (Na–La, Hf–Bi, U–Pu)     | double- $\zeta$ , D95V for H–Ne |
| LANL2TZ     | Sc–Zn, Y–Cd, La, Hf–Hg | HayWadt (Sc–Zn, Y–Cd, La, Hf–Hg) | triple- $\zeta$                 |
| LANL2TZ (f) | Sc–Cu, Y–Ag, La, Hf–Au | HayWadt (Sc–Cu, Y–Ag, La, Hf–Au) | triple- $\zeta$ + polarization  |

## Correlation-consistent Basis Sets

The correlation-consistent basis sets were pioneered by Dunning and co-workers and manifold variants have been developed since. They are among the most widely used for application with correlated wave-function methods and are particularly suited for *basis set extrapolation*. A list of available correlation-consistent basis sets is given in Table 2.22. Relativistic variants are discussed in Section 2.7.3.

Table 2.22: List of available correlation-consistent basis sets.

| Basis Set                      | Elem.                  | ECP | Comment   |
|--------------------------------|------------------------|-----|---|
| cc-pVDZ                        | H–Ar, Ca–Kr            | –   | Dunning correlation-consistent polarized double- $\zeta$    |
| cc-pVTZ                        | H–Ar, Ca–Kr, Y, Ag, Au | –   | Dunning correlation-consistent polarized triple- $\zeta$    |
| cc-pVQZ                        | H–Ar, Ca–Kr            | –   | Dunning correlation-consistent polarized quadruple- $\zeta$ |
| cc-pV5Z                        | H–Ar, Ca–Kr            | –   | Dunning correlation-consistent polarized quintuple- $\zeta$ |
| cc-pV6Z                        | H–He, Be–Ne, Al–Ar     | –   | Dunning correlation-consistent polarized sextuple- $\zeta$  |
| aug-cc-pVDZ                    | H–Ar, Sc–Kr            | –   | cc-pVDZ augmented by diffuse functions                      |
| aug-cc-pVTZ                    | H–Ar, Sc–Kr, Ag, Au    | –   | cc-pVTZ augmented by diffuse functions                      |
| aug-cc-pVQZ                    | H–Ar, Sc–Kr            | –   | cc-pVQZ augmented by diffuse functions                      |
| aug-cc-pV5Z                    | H–Ar, Sc–Kr            | –   | cc-pV5Z augmented by diffuse functions                      |
| aug-cc-pV6Z                    | H–He, B–Ne, Al–Ar      | –   | cc-pV6Z augmented by diffuse functions                      |
| <i>With tight d functions:</i> |                        |     |   |
| cc-pVD (+d) Z                  | Na–Ar                  | –   |   |
| cc-pVT (+d) Z                  | Na–Ar                  | –   |   |
| cc-pVQ (+d) Z                  | Na–Ar                  | –   |   |
| cc-pV5 (+d) Z                  | Na–Ar                  | –   |   |
| aug-cc-pVD (+d) Z              | Al–Ar                  | –   | cc-pVD (+d) Z augmented by diffuse functions                |

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Table 2.22 – continued from previous page

| Basis Set  | Elem.                                 | ECP   | Comment  |
|--|---------------------------------------|---|--|
| aug-cc-pVT (+d) Z  | Al–Ar                                 | –   | cc-pVT (+d) Z augmented by diffuse functions                                 |
| aug-cc-pVQ (+d) Z  | Al–Ar                                 | –   | cc-pVQ (+d) Z augmented by diffuse functions                                 |
| aug-cc-pV5 (+d) Z  | Al–Ar                                 | –   | cc-pV5 (+d) Z augmented by diffuse functions                                 |
| aug-cc-pV6 (+d) Z  | Al–Ar                                 | –   | cc-pV6 (+d) Z augmented by diffuse functions                                 |
| <i>Partially augmented according to Truhlar et al.[47]:</i>  |                                       |   |  |
| apr-cc-pV (Q+d) Z  | H–Ar                                  | –   | Augmented with sp diffuse functions on Li–Ca                                 |
| may-cc-pV (T+d) Z  | H–Ar                                  | –   | Augmented with sp diffuse functions on Li–Ca                                 |
| may-cc-pV (Q+d) Z  | H–Ar                                  | –   | Augmented with spd diffuse functions on Li–Ca                                |
| jun-cc-pV (D+d) Z  | H–Ar                                  | –   | Augmented with sp diffuse functions on Li–Ca                                 |
| jun-cc-pV (T+d) Z  | H–Ar                                  | –   | Augmented with spd diffuse functions on Li–Ca                                |
| jun-cc-pV (Q+d) Z  | H–Ar                                  | –   | Augmented with spdf diffuse functions on Li–Ca                               |
| jul-cc-pV (D+d) Z  | H–Ar                                  | –   | Augmented with spd diffuse functions on Li–Ca                                |
| jul-cc-pV (T+d) Z  | H–Ar                                  | –   | Augmented with spdf diffuse functions on Li–Ca                               |
| jul-cc-pV (Q+d) Z  | H–Ar                                  | –   | Augmented with spdfg diffuse functions on Li–Ca                              |
| maug-cc-pV (D+d) Z   | H–Ar                                  | –   | Equals jun-cc-pV (D+d) Z   |
| maug-cc-pV (T+d) Z   | H–Ar                                  | –   | Equals may-cc-pV (T+d) Z   |
| maug-cc-pV (Q+d) Z   | H–Ar                                  | –   | Equals apr-cc-pV (Q+d) Z   |
| <i>Core-polarized for core-valence electron correlation:</i> |                                       |   |  |
| cc-pCVDZ   | H–Ar, Ca, Ga–Kr                       | –   | Equals cc-pVDZ for H and He  |
| cc-pCVTZ   | H–Ar, Ca, Ga–Kr                       | –   | Equals cc-pVTZ for H and He  |
| cc-pCVQZ   | H–Ar, Ca, Ga–Kr                       | –   | Equals cc-pVQZ for H and He  |
| cc-pCV5Z   | H–Ar, Ca, Ga–Kr                       | –   | Equals cc-pV5Z for H and He  |
| cc-pCV6Z   | H–He, B–Ne, Al–Ar                     | –   | Equals cc-pV6Z for H and He  |
| aug-cc-pCVDZ   | H–Ar, Ga–Kr                           | –   | cc-pCVDZ augmented by diffuse functions, equals<br>aug-cc-pVDZ for H and He  |
| aug-cc-pCVTZ   | H–Ar, Ga–Kr                           | –   | cc-pCVTZ augmented by diffuse functions, equals<br>aug-cc-pVTZ for H and He  |
| aug-cc-pCVQZ   | H–Ar, Ga–Kr                           | –   | cc-pCVQZ augmented by diffuse functions, equals<br>aug-cc-pVQZ for H and He  |
| aug-cc-pCV5Z   | H–Ar, Ga–Kr                           | –   | cc-pCV5Z augmented by diffuse functions, equals<br>aug-cc-pV5Z for H and He  |
| aug-cc-pCV6Z   | H–He, B–Ne, Al–Ar                     | –   | cc-pCV6Z augmented by diffuse functions, equals<br>aug-cc-pV6Z for H and He  |
| <i>Core-polarized with weighted core functions:</i>          |                                       |   |  |
| cc-pwCVDZ  | H–Ar, Ca, Ga–Kr                       | –   | Equals cc-pVDZ for H and He  |
| cc-pwCVTZ  | H–Ar, Ca–Kr, Ag, Au                   | –   | Equals cc-pVTZ for H and He  |
| cc-pwCVQZ  | H–Ar, Ca–Kr                           | –   | Equals cc-pVQZ for H and He  |
| cc-pwCV5Z  | H–Ar, Ca–Kr                           | –   | Equals cc-pV5Z for H and He  |
| aug-cc-pwCVDZ  | H–Ar, Ga–Kr                           | –   | cc-pwCVDZ augmented by diffuse functions, equals<br>aug-cc-pVDZ for H and He |
| aug-cc-pwCVTZ  | H–Ar, Sc–Kr, Ag, Au                   | –   | cc-pwCVTZ augmented by diffuse functions, equals<br>aug-cc-pVTZ for H and He |
| aug-cc-pwCVQZ  | H–Ar, Sc–Kr                           | –   | cc-pwCVQZ augmented by diffuse functions, equals<br>aug-cc-pVQZ for H and He |
| aug-cc-pwCV5Z  | H–Ar, Sc–Kr                           | –   | cc-pwCV5Z augmented by diffuse functions, equals<br>aug-cc-pV5Z for H and He |
| <i>Pseudo-potential (ECP) variants:</i>                      |                                       |   |  |
| cc-pVDZ–PP   | Ca, Cu–Kr, Sr–Xe, Ba,<br>Hf–Rn, Ra, U | SK–MCDHF–RSC<br>(Ca, Cu–Kr, Sr–<br>Xe, Ba, Hf–Ra,<br>U) |  |
| cc-pVTZ–PP   | Ca, Cu–Kr, Sr–Xe, Ba,<br>Hf–Rn, Ra, U | SK–MCDHF–RSC<br>(Ca, Cu–Kr, Sr–<br>Xe, Ba, Hf–Ra,<br>U) |  |
| cc-pVQZ–PP   | Ca, Cu–Kr, Sr–Xe, Ba,<br>Hf–Rn, Ra, U | SK–MCDHF–RSC<br>(Ca, Cu–Kr, Sr–<br>Xe, Ba, Hf–Ra,<br>U) |  |
| cc-pV5Z–PP   | Ca, Cu–Kr, Sr–Xe, Ba,<br>Hf–Rn, Ra    | SK–MCDHF–RSC<br>(Ca, Cu–Kr, Sr–<br>Xe, Ba, Hf–Ra,<br>U) |  |
| aug-cc-pVDZ–PP   | Ca, Cu–Kr, Sr–Xe, Ba,<br>Hf–Rn, Ra    | SK–MCDHF–RSC<br>(Ca, Cu–Kr, Sr–<br>Xe, Ba, Hf–Ra,<br>U) | cc-pVDZ–PP augmented by diffuse functions                                    |

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Table 2.22 – continued from previous page

| Basis Set  | Elem.                              | ECP   | Comment   |
|--|------------------------------------|---|---|
| aug-cc-pVTZ-PP                                     | Ca, Cu–Kr, Sr–Xe, Ba, Hf–Rn, Ra    | SK-MCDHF-RSC (Ca, Cu–Kr, Sr–Xe, Ba, Hf–Ra, U) | cc-pVTZ-PP augmented by diffuse functions                             |
| aug-cc-pVQZ-PP                                     | Ca, Cu–Kr, Sr–Xe, Ba, Hf–Rn, Ra    | SK-MCDHF-RSC (Ca, Cu–Kr, Sr–Xe, Ba, Hf–Ra, U) | cc-pVQZ-PP augmented by diffuse functions                             |
| aug-cc-pV5Z-PP                                     | Ca, Cu–Kr, Sr–Xe, Ba, Hf–Rn, Ra    | SK-MCDHF-RSC (Ca, Cu–Kr, Sr–Xe, Ba, Hf–Ra, U) | cc-pV5Z-PP augmented by diffuse functions                             |
| cc-pCVDZ-PP  | Ca, Sr, Ba, Ra                     | SK-MCDHF-RSC (Ca, Sr, Ba, Ra)                 |   |
| cc-pCVTZ-PP  | Ca, Sr, Ba, Ra                     | SK-MCDHF-RSC (Ca, Sr, Ba, Ra)                 |   |
| cc-pCVQZ-PP  | Ca, Sr, Ba, Ra                     | SK-MCDHF-RSC (Ca, Sr, Ba, Ra)                 |   |
| cc-pCV5Z-PP  | Ca, Sr, Ba, Ra                     | SK-MCDHF-RSC (Ca, Sr, Ba, Ra)                 |   |
| aug-cc-pCVDZ-PP                                    | Ca, Sr, Ba, Ra                     | SK-MCDHF-RSC (Ca, Sr, Ba, Ra)                 | cc-pCVDZ-PP augmented by diffuse functions                            |
| aug-cc-pCVTZ-PP                                    | Ca, Sr, Ba, Ra                     | SK-MCDHF-RSC (Ca, Sr, Ba, Ra)                 | cc-pCVTZ-PP augmented by diffuse functions                            |
| aug-cc-pCVQZ-PP                                    | Ca, Sr, Ba, Ra                     | SK-MCDHF-RSC (Ca, Sr, Ba, Ra)                 | cc-pCVQZ-PP augmented by diffuse functions                            |
| aug-cc-pCV5Z-PP                                    | Ca, Sr, Ba, Ra                     | SK-MCDHF-RSC (Ca, Sr, Ba, Ra)                 | cc-pCV5Z-PP augmented by diffuse functions                            |
| cc-pwCVDZ-PP                                       | Ca, Cu–Kr, Sr–Xe, Ba, Hf–Rn, Ra, U | SK-MCDHF-RSC (Ca, Cu–Kr, Sr–Xe, Ba, Hf–Ra, U) |   |
| cc-pwCVTZ-PP                                       | Ca, Cu–Kr, Sr–Xe, Ba, Hf–Rn, Ra, U | SK-MCDHF-RSC (Ca, Cu–Kr, Sr–Xe, Ba, Hf–Ra, U) |   |
| cc-pwCVQZ-PP                                       | Ca, Cu–Kr, Sr–Xe, Ba, Hf–Rn, Ra, U | SK-MCDHF-RSC (Ca, Cu–Kr, Sr–Xe, Ba, Hf–Ra, U) |   |
| cc-pwCV5Z-PP                                       | Ca, Cu–Kr, Sr–Xe, Ba, Hf–Rn, Ra    | SK-MCDHF-RSC (Ca, Cu–Kr, Sr–Xe, Ba, Hf–Ra, U) |   |
| aug-cc-pwCVDZ-PP                                   | Ca, Cu–Kr, Sr–Xe, Ba, Hf–Rn, Ra    | SK-MCDHF-RSC (Ca, Cu–Kr, Sr–Xe, Ba, Hf–Ra, U) | cc-pwCVDZ-PP augmented by diffuse functions                           |
| aug-cc-pwCVTZ-PP                                   | Ca, Cu–Kr, Sr–Xe, Ba, Hf–Rn, Ra    | SK-MCDHF-RSC (Ca, Cu–Kr, Sr–Xe, Ba, Hf–Ra, U) | cc-pwCVTZ-PP augmented by diffuse functions                           |
| aug-cc-pwCVQZ-PP                                   | Ca, Cu–Kr, Sr–Xe, Ba, Hf–Rn, Ra    | SK-MCDHF-RSC (Ca, Cu–Kr, Sr–Xe, Ba, Hf–Ra, U) | cc-pwCVQZ-PP augmented by diffuse functions                           |
| aug-cc-pwCV5Z-PP                                   | Ca, Cu–Kr, Sr–Xe, Ba, Hf–Rn, Ra    | SK-MCDHF-RSC (Ca, Cu–Kr, Sr–Xe, Ba, Hf–Ra, U) | cc-pwCV5Z-PP augmented by diffuse functions                           |
| <i>Optimized for hyperfine coupling constants:</i> |                                    |   |   |
| aug-cc-pVTZ-J                                      | H, B–F, Al–Cl, Sc–Zn, Se           | –   | Sauer’s basis set for accurate hyperfine coupling                     |
| <i>W4 theory:</i>                                  |                                    |   |   |
| haV (T+d) Z  | H–Ar                               | –   | cc-pVTZ (H–Be, Na, Mg), aug-cc-pVTZ (B–Ne), aug-cc-pVT (+d) Z (Al–Ar) |
| haV (Q+d) Z  | H–Ar                               | –   | cc-pVQZ (H–Be, Na, Mg), aug-cc-pVQZ (B–Ne), aug-cc-pVQ (+d) Z (Al–Ar) |

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Table 2.22 – continued from previous page

| Basis Set   | Elem. | ECP | Comment  |
|-------------|-------|-----|--|
| haV (5+d) Z | H–Ar  | –   | cc-pV5Z (H–Be, Na, Mg), aug-cc-pV5Z (B–Ne),<br>aug-cc-pV5 (+d) Z (Al–Ar) |

## F12 Basis Sets

Special orbital basis sets for *F12 calculations* (larger than the regular D, T, Q-zeta basis sets!). A list of available F12 basis sets is given in Table 2.23. See Table 2.37 for the necessary complementary auxiliary basis sets (CABS).

Table 2.23: F12 basis sets.

| Basis Set                               | Elem.                     | ECP                                    | Comment |
|---|---------------------------|--|---------|
| cc-pVDZ-F12                             | H–Ar                      | –                                      |         |
| cc-pVTZ-F12                             | H–Ar                      | –                                      |         |
| cc-pVQZ-F12                             | H–Ar                      | –                                      |         |
| <i>Core-polarized:</i>                  |                           |  |         |
| cc-pCVDZ-F12                            | Li–Ar                     | –                                      |         |
| cc-pCVTZ-F12                            | Li–Ar                     | –                                      |         |
| cc-pCVQZ-F12                            | Li–Ar                     | –                                      |         |
| <i>Pseudo-potential (ECP) variants:</i> |                           |  |         |
| cc-pVDZ-PP-F12                          | Ga–Kr,<br>In–Xe,<br>Tl–Rn | SK-MCDHF-RSC (Ga–<br>Kr, In–Xe, Tl–Rn) |         |
| cc-pVTZ-PP-F12                          | Ga–Kr,<br>In–Xe,<br>Tl–Rn | SK-MCDHF-RSC (Ga–<br>Kr, In–Xe, Tl–Rn) |         |
| cc-pVQZ-PP-F12                          | Ga–Kr,<br>In–Xe,<br>Tl–Rn | SK-MCDHF-RSC (Ga–<br>Kr, In–Xe, Tl–Rn) |         |

## Atomic Natural Orbital Basis Sets

Atomic natural orbitals are a special class of basis sets. They are represented by the orthonormal set of orbitals that diagonalizes a spherically symmetric, correlated atomic density. The idea is to put as much information as possible into each basis functions such that one obtains the best possible result with the given number of basis functions. This is particularly important for correlated calculations where the number of primitives is less an issue than the number of basis functions. ORCA features some ANO basis sets on the basis of the cc-pV6Z (or pc-4 where missing) basis set primitives.[48] These are very accurate and significantly better than the cc-pVnZ counterparts for the same number of basis functions (but much larger number of primitives). A list of available ANO basis sets is given in Table 2.24.

### Note

- **aug-ANO-pVnZ:** full augmentation with spd, spdf, spdfg set of polarization functions. Almost as expensive as the next higher basis set. In fact, aug-ANO-pVnZ = ANO-pV(n + 1)Z with the highest angular momentum polarization function deleted.
- **saug-ANO-pVnZ:** augmentation with a single set of sp functions. Greatly enhances the accuracy of the SCF energies but not for correlation energies.

Table 2.24: Available atomic natural orbital (ANO) basis sets.

| Basis Set     | Elem.          | ECP | Comment  |
|---------------|----------------|-----|--|
| ANO-SZ        | H-Ar,<br>Sc-Zn | –   |  |
| ANO-pVDZ      | H-Ar,<br>Sc-Zn | –   |  |
| ANO-pVTZ      | H-Ar,<br>Sc-Zn | –   |  |
| ANO-pVQZ      | H-Ar,<br>Sc-Zn | –   |  |
| ANO-pV5Z      | H-Ar,<br>Sc-Zn | –   |  |
| ANO-pV6Z      | H-Ar,<br>Sc-Zn | –   |  |
| aug-ANO-pVDZ  | H-Ar,<br>Sc-Zn | –   | ANO-pVDZ augmented by diffuse functions                    |
| aug-ANO-pVTZ  | H-Ar,<br>Sc-Zn | –   | ANO-pVTZ augmented by diffuse functions                    |
| aug-ANO-pVQZ  | H-Ar,<br>Sc-Zn | –   | ANO-pVQZ augmented by diffuse functions                    |
| aug-ANO-pV5Z  | H-Ar,<br>Sc-Zn | –   | ANO-pV5Z augmented by diffuse functions                    |
| saug-ANO-pVDZ | H-Ar,<br>Sc-Zn | –   | ANO-pVDZ augmented by a single set of diffuse sp functions |
| saug-ANO-pVTZ | H-Ar,<br>Sc-Zn | –   | ANO-pVTZ augmented by a single set of diffuse sp functions |
| saug-ANO-pVQZ | H-Ar,<br>Sc-Zn | –   | ANO-pVQZ augmented by a single set of diffuse sp functions |
| saug-ANO-pV5Z | H-Ar,<br>Sc-Zn | –   | ANO-pV5Z augmented by a single set of diffuse sp functions |

## Efficient Calculations with ANO Basis Sets

Usually, ANO basis sets are “generally contracted” which means that for any given angular momentum all primitives contribute to all basis functions. Since the concept of ANOs only makes sense if the underlying set of primitives is large, the calculations readily become very expensive unless special precaution is taken in the integral evaluation algorithms. ORCA features special algorithms for ANO basis sets together with accurate ANO basis sets for non-relativistic calculations. However, even then the integral evaluation is so expensive that efficiency can only be realized if all integrals are stored on disk and are re-used as needed.

Currently, the use of ANOs is restricted to the *built-in ANO basis sets*. These are built upon the cc-pV6Z primitives and hence, the calculations take significant time.

### Hint

Geometry optimizations with ANOs are discouraged; they will be *very* inefficient.

The use of ANOs is recommended in the following way:

```
! ano-pVTZ Conv TightSCF CCSD(T)
%maxcore 2000
* int 0 1
C 0 0 0 0 0 0
O 1 0 0 1.2 0 0
H 1 2 0 1.1 120 0
H 1 2 3 1.1 120 180
*
```

This yields:

```
ano-pVTZ:
E(SCF) = -113.920388785
E(corr) = -0.427730189
```

Compare to the cc-pVTZ value of:

```
cc-pVTZ:
E(SCF) = -113.911870901
E(corr) = -0.421354947
```

Thus, the ANO-based SCF energy is ca. 8–9 mEh lower and the correlation energy almost 2 mEh lower than with the cc-basis set of the same size. Usually, the ANO results are much closer to the basis set limit than the cc-results. Also, ANO values extrapolate very well (see section [Automatic extrapolation to the basis set limit](#))

Importantly, the integrals are all stored in this job. Depending on your system and your patience, this may be possible up to 300–500 basis functions. The ORCA correlation modules have been rewritten such that they deal efficiently with these stored integrals. Thus, we might as well have used ! MO-CCSD(T) or ! AO-CCSD(T), both of which would perform well.

Yet, the burden of generating and storing all four-index integrals quickly becomes rather heavy. Hence, the combination of ANO basis sets with the RI-JK technique is particularly powerful and efficient. For example:

```
! ano-pVTZ cc-pVTZ/JK RI-JK Conv TightSCF RI-CCSD(T)
```

For the SCF, this works very well and allows for much larger ANO based calculations to be done efficiently. Also, RI-MP2 can be done very efficiently in this way. However, for higher order correlation methods such as CCSD(T) the logical choice would be RI-CCSD(T) which is distinctly less efficient than the AO or MO based CCSD(T) (roughly a factor of two slower). Hence, ORCA implements a hybrid method where the RI approximation is used to generate all four index integrals. This is done via the “RI-AO” keyword:

```
! ano-pVTZ cc-pVTZ/JK RI-AO Conv TightSCF AO-CCSD(T)
```

In this case either AO-CCSD(T) or MO-CCSD(T) would both work well. This does not solve the storage bottleneck with respect to the four index integrals of course. If this becomes a real issue, then RI-CCSD(T) is mandatory. The error in the total energy is less than 0.1 mEh in the present example.

### Warning

With conventional RI calculations the use of a second fit basis set is not possible and inconsistent results will be obtained. Hence, stick to one auxiliary basis!

## Miscellaneous and Specialized Basis Sets

A list of further available specialized and miscellaneous basis sets is given in [Table 2.25](#).

Table 2.25: Collection of available miscellaneous and specialized basis sets.

| Basis Set          | Elem.                    | ECP                                  | Comment   |
|--------------------|--------------------------|--------------------------------------|---|
| D95                | H, Li, B-<br>Ne, Al-Cl   | –                                    | Dunning’s double- $\zeta$ basis set   |
| D95p               | H, Li, B-<br>Ne, Al-Cl   | –                                    | Polarized version of D95  |
| EPR-II             | H, B-F                   | –                                    | Barone’s double- $\zeta$ basis set for EPR calculations   |
| EPR-III            | H, B-F                   | –                                    | Barone’s triple- $\zeta$ basis set for EPR calculations   |
| IGLO-II            | H, B-F,<br>Al-Cl         | –                                    | Kutzelnigg’s basis set for NMR and EPR calculations.  |
| IGLO-III           | H, B-F,<br>Al-Cl         | –                                    | Kutzelnigg’s larger basis set for NMR and EPR calculations.   |
| UGBS               | H-Th,<br>Pu-Am,<br>Cf-Lr | –                                    | Universal Gaussian basis set.   |
| CP                 | Sc-Zn                    | –                                    |   |
| CP (PPP)           | Sc-Zn                    | –                                    |   |
| Wachters+f         | Sc-Cu                    | –                                    |   |
| W1- <i>mtsmall</i> | H-Ar                     | –                                    | W1 theory basis set   |
| W1-DZ              | H-Ar                     | –                                    | W1 theory basis set   |
| W1-TZ              | H-Ar                     | –                                    | W1 theory basis set   |
| W1-QZ              | H-Ar                     | –                                    | W1 theory basis set   |
| W1-Opt             | H-Ar                     | –                                    | W1 theory basis set   |
| MINI               | H-Ca                     | –                                    | Huzinaga’s minimal basis set.   |
| MINIS              | H-Ca                     | –                                    | Scaled version of the MINI  |
| MIDI               | H-Na,<br>Al-K            | –                                    | Huzinaga’s valence double- $\zeta$ basis set  |
| MINIX              | H-Lr                     | def-ECP (Rb-Lr)                      | Combination of small basis sets by Grimme (see Table 3.30). Used in <i>HF-3c</i> .  |
| def2-mSVP          | H-Lr                     | def2-ECP (Rb-Rn),<br>def-ECP (Fr-Lr) | Used in <i>PBEh-3c</i> and <i>B3LYP-3c</i>  |
| def2-mTZVP         | H-Lr                     | def2-ECP (Rb-Rn),<br>def-ECP (Fr-Lr) | Used in <i>B97-3c</i>   |
| def2-mTZVPP        | H-Lr                     | def2-ECP (Rb-Rn),<br>def-ECP (Fr-Lr) | Used in <i>r<sup>2</sup>SCAN-3c</i>   |
| vDZP               | H-Rn                     | vDZP-ECP (B-Rn)                      | Molecule-optimized polarized valence double- $\zeta$ basis set by Grimme et al. Used in <i><math>\omega</math>B97X-3c</i> . <sup>[49]</sup> |

## 2.7.3 Relativistic Basis Sets

Scalar-relativistic calculations with the *DKH*, *ZORA* or *X2C* approaches typically require specifically optimized or recontracted basis sets – see *Basis Sets in Relativistic Calculations* for details. ORCA provides various suitable basis sets for such calculations like the recontracted *Karlsruhe*, the *SARC*, and *SARC2*, and various optimized all-electron *correlation-consistent* basis sets. Suitable auxiliary basis options like *SARC/J* or *AutoAux* can be found in Section 2.7.4.

### Recontracted Ahlrichs Basis Sets

A list of available relativistically recontracted variants of the original Ahlrichs basis sets is given in Table 2.26. Refer to the section *Ahlrichs Basis Sets* for the origin of the legacy definitions with the prefix “old-“.

Table 2.26: Relativistically recontracted Ahlrichs basis sets. RH = relativistic Hamiltonian.

| Basis Set                                    | Elem. | RH   | Comment |
|--|-------|------|---------|
| DKH-SV (P)                                   | H-Kr  | DKH2 |         |
| DKH-SVP                                      | H-Kr  | DKH2 |         |
| DKH-TZV (P)                                  | H-Kr  | DKH2 |         |
| DKH-TZVP                                     | H-Kr  | DKH2 |         |
| DKH-TZVPP                                    | H-Kr  | DKH2 |         |
| DKH-QZVP                                     | H-Kr  | DKH2 |         |
| DKH-QZVPP                                    | H-Kr  | DKH2 |         |
| ZORA-SV (P)                                  | H-Kr  | ZORA |         |
| ZORA-SVP                                     | H-Kr  | ZORA |         |
| ZORA-TZV (P)                                 | H-Kr  | ZORA |         |
| ZORA-TZVP                                    | H-Kr  | ZORA |         |
| ZORA-TZVPP                                   | H-Kr  | ZORA |         |
| ZORA-QZVP                                    | H-Kr  | ZORA |         |
| ZORA-QZVPP                                   | H-Kr  | ZORA |         |
| <i>Legacy definitions (not recommended!)</i> |       |      |         |
| old-DKH-SV (P)                               | H-I   | DKH2 |         |
| old-DKH-SVP                                  | H-I   | DKH2 |         |
| old-DKH-TZV (P)                              | H-I   | DKH2 |         |
| old-DKH-TZVP                                 | H-I   | DKH2 |         |
| old-DKH-TZVPP                                | H-I   | DKH2 |         |
| old-ZORA-SV (P)                              | H-I   | ZORA |         |
| old-ZORA-SVP                                 | H-I   | ZORA |         |
| old-ZORA-TZV (P)                             | H-I   | ZORA |         |
| old-ZORA-TZVP                                | H-I   | ZORA |         |
| old-ZORA-TZVPP                               | H-I   | ZORA |         |

## Recontracted Karlsruhe def2 Basis Sets

A list of available adapted *DKH* and *ZORA* versions of the def2 basis sets (i.e., for the all-electron def2 basis sets) is given in Table 2.27. These basis sets retain the original def2 exponents but have only one contracted function per angular momentum (and hence are somewhat larger), with contraction coefficients suitable for the respective scalar relativistic Hamiltonian. These basis sets can be combined with the *SARC* and *SARC2* basis sets for the heavier elements.

Table 2.27: Relativistically recontracted Karlsruhe basis sets. RH = relativistic Hamiltonian.

| Basis Set   | Elem. | RH   | Comment |
|---|-------|------|---------|
| DKH-def2-SVP  | H-Kr  | DKH2 |         |
| DKH-def2-SV (P)   | H-Kr  | DKH2 |         |
| DKH-def2-TZVP   | H-Kr  | DKH2 |         |
| DKH-def2-TZVP (-f)  | H-Kr  | DKH2 |         |
| DKH-def2-TZVPP  | H-Kr  | DKH2 |         |
| DKH-def2-QZVPP  | H-Kr  | DKH2 |         |
| ZORA-def2-SVP   | H-Kr  | ZORA |         |
| ZORA-def2-SV (P)  | H-Kr  | ZORA |         |
| ZORA-def2-TZVP  | H-Kr  | ZORA |         |
| ZORA-def2-TZVP (-f)                                       | H-Kr  | ZORA |         |
| ZORA-def2-TZVPP   | H-Kr  | ZORA |         |
| ZORA-def2-QZVPP   | H-Kr  | ZORA |         |
| <i>Minimally augmented (scheme by Truhlar et al.[17])</i> |       |      |         |
| ma-DKH-def2-SVP   | H-Kr  | DKH2 |         |
| ma-DKH-def2-SV (P)  | H-Kr  | DKH2 |         |
| ma-DKH-def2-TZVP  | H-Kr  | DKH2 |         |
| ma-DKH-def2-TZVP (-f)                                     | H-Kr  | DKH2 |         |
| ma-DKH-def2-TZVPP   | H-Kr  | DKH2 |         |
| ma-DKH-def2-QZVPP   | H-Kr  | DKH2 |         |
| ma-ZORA-def2-SVP  | H-Kr  | ZORA |         |
| ma-ZORA-def2-SV (P)                                       | H-Kr  | ZORA |         |
| ma-ZORA-def2-TZVP   | H-Kr  | ZORA |         |
| ma-ZORA-def2-TZVP (-f)                                    | H-Kr  | ZORA |         |
| ma-ZORA-def2-TZVPP  | H-Kr  | ZORA |         |
| ma-ZORA-def2-QZVPP  | H-Kr  | ZORA |         |

## SARC Basis Sets

Segmented all-electron relativistically contracted (SARC) basis sets for use with the DKH2 and ZORA Hamiltonians.[50, 51, 52, 53, 54, 55] A list of available SARC basis sets is given in Table 2.28.

### Tip

Specifically for wavefunction-based calculations of lanthanide systems we recommend the more heavily polarized *SARC2 basis sets* [56].

Table 2.28: Relativistic SARC basis sets. RH = relativistic Hamiltonian.

| Basis Set       | Elem.           | RH   | Comment |
|-----------------|-----------------|------|---------|
| SARC-DKH-SVP    | Hf-Hg           | DKH2 |         |
| SARC-DKH-TZVP   | Rb-Rn,<br>Ac-Lr | DKH2 |         |
| SARC-DKH-TZVPP  | Rb-Rn,<br>Ac-Lr | DKH2 |         |
| SARC-ZORA-SVP   | Hf-Hg           | ZORA |         |
| SARC-ZORA-TZVP  | Rb-Rn,<br>Ac-Lr | ZORA |         |
| SARC-ZORA-TZVPP | Rb-Rn,<br>Ac-Lr | ZORA |         |

### Note

*SARC/J* is the general-purpose Coulomb-fitting auxiliary for all SARC orbital basis sets.

## SARC2 Basis Sets

SARC basis sets of valence quadruple-zeta quality for lanthanides, with NEVPT2-optimized (3g2h) polarization functions (SARC2).[56] Suitable for accurate calculations using correlated wavefunction methods. A list of available SARC2 basis sets is given in Table 2.29.

Table 2.29: Relativistic SARC2 basis sets. RH = relativistic Hamiltonian.

| Basis Set       | Elem. | ECP  | Comment |
|-----------------|-------|------|---------|
| SARC2-DKH-QZV   | La-Lu | DKH2 |         |
| SARC2-DKH-QZVP  | La-Lu | DKH2 |         |
| SARC2-ZORA-QZV  | La-Lu | ZORA |         |
| SARC2-ZORA-QZVP | La-Lu | ZORA |         |

### Note

Each basis set has a large dedicated /JK auxiliary basis set for simultaneous Coulomb and exchange fitting (cf. Table 2.35).

## Karlsruhe x2c Basis Sets

For calculations with the X2C Hamiltonian, all-electron basis sets up to Rn are available.[57] The “-s” variants, e.g. x2c-TZVPall-s, are augmented with additional tight functions for NMR shielding calculations.[58] The “-2c” variants, e.g. x2c-TZVPall-2c, are intended for two-component calculations including spin-orbit coupling (**Note that two-component calculations are not implemented in ORCA**). A list of available basis sets of this family is given in Table 2.30.

### Tip

The x2c/J and AutoAux auxiliary basis set options can be used for these basis sets.

Table 2.30: Karlsruhe basis sets optimized for the x2c Hamiltonian.[57] RH = relativistic Hamiltonian.

| Basis Set  | Elem. | RH     | Comment |
|--|-------|--------|---------|
| x2c-SV(P)all   | H-Rn  | X2C    |         |
| x2c-SVPall   | H-Rn  | X2C    |         |
| x2c-TZVPall  | H-Rn  | X2C    |         |
| x2c-TZVPPall   | H-Rn  | X2C    |         |
| x2c-QZVPall  | H-Rn  | X2C    |         |
| x2c-QZVPPall   | H-Rn  | X2C    |         |
| <i>NMR shielding optimized</i> [58]                          |       |        |         |
| x2c-SV(P)all-s   | H-Rn  | X2C    |         |
| x2c-SVPall-s   | H-Rn  | X2C    |         |
| x2c-TZVPall-s  | H-Rn  | X2C    |         |
| x2c-TZVPPall-s   | H-Rn  | X2C    |         |
| x2c-QZVPall-s  | H-Rn  | X2C    |         |
| x2c-QZVPPall-s   | H-Rn  | X2C    |         |
| <i>Two-component variants (no matching Hamiltonian yet!)</i> |       |        |         |
| x2c-SV(P)all-2c  | H-Rn  | SO-X2C |         |
| x2c-SVPall-2c  | H-Rn  | SO-X2C |         |
| x2c-TZVPall-2c   | H-Rn  | SO-X2C |         |
| x2c-TZVPPall-2c  | H-Rn  | SO-X2C |         |
| x2c-QZVPall-2c   | H-Rn  | SO-X2C |         |
| x2c-QZVPPall-2c  | H-Rn  | SO-X2C |         |
| x2c-QZVPall-2c-s   | H-Rn  | SO-X2C |         |
| x2c-QZVPPall-2c-s  | H-Rn  | SO-X2C |         |

## Relativistic Sapporo Basis Sets

A list of relativistic variants of the *Sapporo basis sets* that were optimized for the DKH3 Hamiltonian and finite nucleus are given in Table 2.31.

Table 2.31: Relativistic Sapporo basis sets. RH = relativistic Hamiltonian.

| Basis Set          | Elem. | RH   | Comment                               |
|--------------------|-------|------|---------------------------------------|
| Sapporo-DKH3-DZP-2 | K-Rn  | DKH3 | Optimized for DKH3 and finite nucleus |
| Sapporo-DKH3-TZP-2 | K-Rn  | DKH3 |                                       |
| Sapporo-DKH3-QZP-2 | K-Rn  | DKH3 |                                       |

## Relativistic Correlation-Consistent Basis Sets

A list of relativistic variants of the *correlation-consistent basis sets* is given in Table 2.32.

Table 2.32: Relativistic correlation-consistent basis sets. RH = relativistic Hamiltonian.

| Basis Set        | Elem.  | RH   | Comment   |
|------------------|--|------|---|
| cc-pVDZ-DK       | H-Ar,<br>Sc-Kr                               | DKH2 |   |
| cc-pVTZ-DK       | H-Ar,<br>Sc-Kr,<br>Y-Xe,<br>Hf-Rn            | DKH2 |   |
| cc-pVQZ-DK       | H-Ar,<br>Sc-Kr,<br>In-Xe,<br>Tl-Rn           | DKH2 |   |
| cc-pV5Z-DK       | H-Ar,<br>Sc-Kr                               | DKH2 |   |
| cc-pVDZ-DK3      | U  | DKH3 | For use with 3rd-order DKH  |
| cc-pVTZ-DK3      | U  | DKH3 |   |
| cc-pVQZ-DK3      | U  | DKH3 |   |
| aug-cc-pVDZ-DK   | H-Ar,<br>Sc-Kr                               | DKH2 | cc-pVDZ-DK augmented by diffuse functions                                       |
| aug-cc-pVTZ-DK   | H-Ar,<br>Sc-Kr,<br>Y-Xe,<br>Hf-Rn            | DKH2 | cc-pVTZ-DK augmented by diffuse functions                                       |
| aug-cc-pVQZ-DK   | H-Ar,<br>Sc-Kr,<br>In-Xe,<br>Tl-Rn           | DKH2 | cc-pVQZ-DK augmented by diffuse functions                                       |
| aug-cc-pV5Z-DK   | H-Ar,<br>Sc-Kr                               | DKH2 | cc-pV5Z-DK augmented by diffuse functions                                       |
| cc-pwCVDZ-DK     | H-Be,<br>Na-Mg,<br>Ca-Zn                     | DKH2 | Equals cc-pVDZ-DK for H and He  |
| cc-pwCVTZ-DK     | H-Be,<br>Na-Mg,<br>Ca-Zn,<br>Y-Xe,<br>Hf-Rn  | DKH2 | Equals cc-pVTZ-DK for H and He  |
| cc-pwCVQZ-DK     | H-Be,<br>Na-Mg,<br>Ca-Zn,<br>In-Xe,<br>Tl-Rn | DKH2 | Equals cc-pVQZ-DK for H and He  |
| cc-pwCV5Z-DK     | H-Be,<br>Na-Mg,<br>Ca-Zn                     | DKH2 | Equals cc-pV5Z-DK for H and He  |
| cc-pwCVDZ-DK3    | U  | DKH3 |   |
| cc-pwCVTZ-DK3    | U  | DKH3 |   |
| cc-pwCVQZ-DK3    | U  | DKH3 |   |
| aug-cc-pwCVDZ-DK | H-Be,<br>Na-Mg,<br>Sc-Zn                     | DKH3 | cc-pwCVDZ-DK augmented by diffuse functions, equals aug-cc-pVDZ-DK for H and He |
| aug-cc-pwCVTZ-DK | H-Be,<br>Na-Mg,<br>Sc-Zn,<br>Y-Xe,<br>Hf-Rn  | DKH2 | cc-pwCVTZ-DK augmented by diffuse functions, equals aug-cc-pVTZ-DK for H and He |
| aug-cc-pwCVQZ-DK | H-Be,<br>Na-Mg,<br>Sc-Zn,<br>In-Xe,<br>Tl-Rn | DKH2 | cc-pwCVQZ-DK augmented by diffuse functions, equals aug-cc-pVQZ-DK for H and He |
| aug-cc-pwCV5Z-DK | H-Be,<br>Na-Mg,<br>Sc-Zn                     | DKH2 | cc-pwCV5Z-DK augmented by diffuse functions, equals aug-cc-pV5Z-DK for H and He |



## Relativistically Contracted ANO Basis Sets

The relativistic contracted ANO basis sets of Roos and coworkers were developed for the DKH2 Hamiltonian. The full list is given in Table 2.33.

Table 2.33: Relativistic contracted ANO basis sets. RH = relativistic Hamiltonian.

| Basis Set    | Elem. | RH   | Comment   |
|--------------|-------|------|---|
| ANO-RCC-Full | H-Cm  | DKH2 | Complete ANO-RCC basis sets.                    |
| ANO-RCC-DZP  | H-Cm  | DKH2 | Double- $\zeta$ contraction of ANO-RCC-Full.    |
| ANO-RCC-TZP  | H-Cm  | DKH2 | Triple- $\zeta$ contraction of ANO-RCC-Full.    |
| ANO-RCC-QZP  | H-Cm  | DKH2 | Quadruple- $\zeta$ contraction of ANO-RCC-Full. |

## 2.7.4 Auxiliary Basis Sets

*Resolution-of-the-identity (RI)* techniques can be used to speed up various types of calculations. Any RI method requires the definition of a reasonable auxiliary basis set in addition to the chosen *orbital basis set*. ORCA provides various built-in auxiliary basis set options for *AuxJ*, *AuxJK*, *AuxC*, and *CABS* and an automatic auxiliary basis set generation called *AutoAux*. Auxiliary basis sets can further be read from external files as described in Section 2.7.9.

### Note

The distinction between *AuxJ*, *AuxJK*, *AuxC*, and *CABS*, as well as how to correctly assign them, is *explained above*.

### Coulomb-fitting auxiliary basis sets (*AuxJ*)

The auxiliary basis sets listed in Table 2.34 are suitable for the *RI-J*, *RIJDX/RIJONX*, and *RIJCOSX* approximations.

Table 2.34: Available Coulomb-fitting auxiliary basis sets.

| Keyword       | Elements    | Comment  |
|---------------|-------------|--|
| def2/J        | H-Lr        | Weigend's "universal" Coulomb-fitting basis suitable for all <i>def2</i> and <i>def</i> type basis sets. Assumes the use of ECPs beyond Kr (do not use with DKH/ZORA/X2C).   |
| def2-mTZVP/J  | H-Lr        |  |
| def2-mTZVPP/J | H-Lr        |  |
| x2c/J         | H-Rn        | Weigend's Coulomb-fitting basis for the all-electron <i>x2c-XVPall</i> basis sets  |
| SARC/J        | H-Rn, Ac-Lr | General-purpose Coulomb-fitting basis set for all-electron calculations. Consists of the decontracted <i>def2/J</i> up to Kr and of our own auxiliary basis sets for the rest of the periodic table. Appropriate for use in DKH or ZORA calculations with the <i>recontracted versions of the all-electron def2</i> basis sets (up to Kr) and the <i>SARC</i> basis sets for the heavier elements. |

### Coulomb- and exchange-fitting auxiliary basis sets (*AuxJK*)

The auxiliary basis sets listed in Table 2.35 are optimized for the *RI-JK* approximation. They can safely be used for *RI-J*, *RIJDX/RIJONX*, or *RIJCOSX*, but in that case they must be assigned to *AuxJ* via the `%basis` block.

Table 2.35: Available Coulomb- and exchange-fitting auxiliary basis sets.

| Keyword            | Elements             | Comment   |
|--------------------|----------------------|---|
| def2/JK            | H–Rn                 | Coulomb+Exchange fitting for all <i>def2</i> basis sets |
| def2/JKsmall       | H–Ra, Th–Lr          | reduced version of <i>def2/JK</i>                       |
| cc-pVTZ/JK         | H, B–F, Al–Cl, Ga–Br | For use with the respective cc-pVnZ orbital basis       |
| cc-pVQZ/JK         | H, B–F, Al–Cl, Ga–Br |   |
| cc-pV5Z/JK         | H, B–F, Al–Cl, Ga–Br |   |
| aug-cc-pVTZ/JK     | H, B–F, Al–Cl, Ga–Br |   |
| aug-cc-pVQZ/JK     | H, B–F, Al–Cl, Ga–Br |   |
| aug-cc-pV5Z/JK     | H, B–F, Al–Cl, Ga–Br |   |
| SARC2-DKH-QZV/JK   | La–Lu                | For use with the respective aug-cc-pVnZ orbital basis   |
| SARC2-DKH-QZVP/JK  | La–Lu                |   |
| SARC2-ZORA-QZV/JK  | La–Lu                |   |
| SARC2-ZORA-QZVP/JK | La–Lu                |   |

## Auxiliary basis sets for correlated methods (AuxC)

The available auxiliary basis sets suitable for post-(CAS)SCF dynamical electron correlation methods are listed in Table 2.36.

Table 2.36: Available auxiliary basis sets for correlated methods.

| Keyword               | Elements                  | Comment  |
|-----------------------|---------------------------|--|
| def2-SVP/C            | H–Rn                      | For use with the respective def2 orbital basis   |
| def2-TZVP/C           | H–Rn                      |  |
| def2-TZVPP/C          | H–Rn                      |  |
| def2-QZVPP/C          | H–Rn                      |  |
| def2-SVPD/C           | H–La, Hf–Rn               |  |
| def2-TZVPD/C          | H–La, Hf–Rn               |  |
| def2-TZVPPD/C         | H–La, Hf–Rn               |  |
| def2-QZVPPD/C         | H–La, Hf–Rn               |  |
| cc-pVDZ/C             | H–Ar, Ga–Kr               | For use with the respective cc-pVnZ orbital basis  |
| cc-pVTZ/C             | H–Ar, Sc–Kr               |  |
| cc-pVQZ/C             | H–Ar, Sc–Kr               |  |
| cc-pV5Z/C             | H–Ar, Ga–Kr               |  |
| cc-pV6Z/C             | H–He, B–Ne, Al–Ar         | For use with the respective aug-cc-pVnZ orbital basis  |
| aug-cc-pVDZ/C         | H–He, Be–Ne, Mg–Ar, Ga–Kr |  |
| aug-cc-pVTZ/C         | H–He, Be–Ne, Mg–Ar, Sc–Kr |  |
| aug-cc-pVQZ/C         | H–He, Be–Ne, Mg–Ar, Sc–Kr |  |
| aug-cc-pV5Z/C         | H–Ne, Al–Ar, Ga–Kr        |  |
| aug-cc-pV6Z/C         | H–He, B–Ne, Al–Ar         |  |
| cc-pwCVDZ/C           | H–He, B–Ne, Al–Ar, Ga–Kr  | For use with the respective cc-pwCVnZ orbital basis, equals cc-pV\$N\$Z/C for H and He         |
| cc-pwCVTZ/C           | H–He, B–Ne, Al–Ar, Sc–Kr  |  |
| cc-pwCVQZ/C           | H–He, B–Ne, Al–Ar, Ga–Kr  |  |
| cc-pwCV5Z/C           | H–Ne, Al–Ar               |  |
| aug-cc-pwCVDZ/C       | H–He, B–Ne, Al–Ar, Ga–Kr  | For use with the respective aug-cc-pwCVnZ orbital basis, equals aug-cc-pV\$N\$Z/C for H and He |
| aug-cc-pwCVTZ/C       | H–He, B–Ne, Al–Ar, Sc–Kr  |  |
| aug-cc-pwCVQZ/C       | H–He, B–Ne, Al–Ar, Ga–Kr  |  |
| aug-cc-pwCV5Z/C       | H–Ne, Al–Ar               |  |
| cc-pVDZ-PP/C          | Cu–Kr, Y–Xe, Hf–Rn        | For use with the respective cc-pVnZ-PP orbital basis   |
| cc-pVTZ-PP/C          | Cu–Kr, Y–Xe, Hf–Rn        |  |
| cc-pVQZ-PP/C          | Cu–Kr, Y–Xe, Hf–Rn        |  |
| aug-cc-pVDZ-PP/C      | Cu–Kr, Y–Xe, Hf–Rn        | For use with the respective aug-cc-pVnZ-PP orbital basis                                       |
| aug-cc-pVTZ-PP/C      | Cu–Kr, Y–Xe, Hf–Rn        |  |
| aug-cc-pVQZ-PP/C      | Cu–Kr, Y–Xe, Hf–Rn        |  |
| cc-pwCVDZ-PP/C        | Cu–Kr, Y–Xe, Hf–Rn        | For use with the respective cc-pwCVnZ-PP orbital basis   |
| cc-pwCVTZ-PP/C        | Cu–Kr, Y–Xe, Hf–Rn        |  |
| cc-pwCVQZ-PP/C        | Cu–Kr, Y–Xe, Hf–Rn        |  |
| aug-cc-pwCVDZ-PP/C    | Cu–Kr, Y–Xe, Hf–Rn        | For use with the respective aug-cc-pwCVnZ-PP orbital basis                                     |
| aug-cc-pwCVTZ-PP/C    | Cu–Kr, Y–Xe, Hf–Rn        |  |
| aug-cc-pwCVQZ-PP/C    | Cu–Kr, Y–Xe, Hf–Rn        |  |
| cc-pVDZ-F12-MP2Fit    | H–Ar                      | For use with the respective cc-pVnZ-F12 orbital basis  |
| cc-pVTZ-F12-MP2Fit    | H–Ar                      |  |
| cc-pVQZ-F12-MP2Fit    | H–Ar                      |  |
| cc-pVDZ-PP-F12-MP2Fit | Ga–Kr, In–Xe, Tl–Rn       | For use with the respective cc-pVnZ-PP-F12 orbital basis                                       |
| cc-pVTZ-PP-F12-MP2Fit | Ga–Kr, In–Xe, Tl–Rn       |  |
| cc-pVQZ-PP-F12-MP2Fit | Ga–Kr, In–Xe, Tl–Rn       |  |
| cc-pCVDZ-F12-MP2Fit   | Li–Ar                     | For use with the respective cc-pCVnZ-F12 orbital basis   |
| cc-pCVTZ-F12-MP2Fit   | Li–Ar                     |  |

continues on next page

Table 2.36 – continued from previous page

| Keyword             | Elements | Comment |
|---------------------|----------|---------|
| cc-pCVQZ-F12-MP2Fit | Li–Ar    |         |

## Complementary auxiliary basis sets for F12 (CABS)

The available CABS options for *F12 methods* are listed in Table 2.37.

Table 2.37: Available complementary auxiliary basis sets for F12 methods.

| Keyword                | Elements            | Comment  |
|------------------------|---------------------|--|
| cc-pVDZ-F12-CABS       | H, B–Ne, Al–Ar      | For use with the respective cc-pVnZ-F12 orbital basis          |
| cc-pVTZ-F12-CABS       | H, B–Ne, Al–Ar      |  |
| cc-pVQZ-F12-CABS       | H, B–Ne, Al–Ar      |  |
| cc-pVDZ-F12-OptRI      | H–Ar                |  |
| cc-pVTZ-F12-OptRI      | H–Ar                |  |
| cc-pVQZ-F12-OptRI      | H–Ar                | Identical to the cc-pVnZ-F12-CABS basis above                  |
| cc-pVDZ-PP-F12-OptRI   | Ga–Kr, In–Xe, Tl–Rn |  |
| cc-pVTZ-PP-F12-OptRI   | Ga–Kr, In–Xe, Tl–Rn |  |
| cc-pVQZ-PP-F12-OptRI   | Ga–Kr, In–Xe, Tl–Rn | For use with the respective cc-pVnZ-PP-F12 orbital basis       |
| aug-cc-pVDZ-PP-OptRI   | Cu–Zn, Ag–Cd, Au–Hg |  |
| aug-cc-pVTZ-PP-OptRI   | Cu–Zn, Ag–Cd, Au–Hg |  |
| aug-cc-pVQZ-PP-OptRI   | Cu–Zn, Ag–Cd, Au–Hg |  |
| aug-cc-pV5Z-PP-OptRI   | Cu–Zn, Ag–Cd, Au–Hg |  |
| cc-pCVDZ-F12-OptRI     | Li–Ar               | For use with the respective cc-pCVnZ-PP-F12 orbital basis      |
| cc-pCVTZ-F12-OptRI     | Li–Ar               |  |
| cc-pCVQZ-F12-OptRI     | Li–Ar               |  |
| aug-cc-pwCVDZ-PP-OptRI | Cu–Zn, Ag–Cd, Au–Hg | For use with the respective aug-cc-pwCVnZ-PP-F12 orbital basis |
| aug-cc-pwCVTZ-PP-OptRI | Cu–Zn, Ag–Cd, Au–Hg |  |
| aug-cc-pwCVQZ-PP-OptRI | Cu–Zn, Ag–Cd, Au–Hg |  |
| aug-cc-pwCV5Z-PP-OptRI | Cu–Zn, Ag–Cd, Au–Hg |  |

## Automatic Generation of Auxiliary Basis Sets (AutoAux)

If no auxiliary basis set is available for your chosen orbital basis set, one can be generated automatically by ORCA using the keyword `AutoAux`. This is specified as any other fitting basis set: as a value to the `AuxJ/AuxJK/AuxC` variables in the `%basis` block or as a separate keyword in the simple input line (in which case all three Aux slots are populated with identical fitting basis sets). `AutoAux` can also be assigned to individual elements or atoms – see sections *Assigning or Adding Basis Functions to an Element* and *Assigning or Adding Basis Functions to Individual Atoms*. The generated basis sets can be used for Coulomb, exchange and correlation fitting and are as accurate as the optimized auxiliary basis sets at the cost of being up to twice as large.[59] The available settings for `AutoAux` are given in Table 2.41 with their default values.

### Note

The generation procedure in ORCA 3.1 was significantly different and does not produce the same results! For compatibility, the old version is still accessible via the setting `OldAutoAux true` in the `%basis` block.

Note that if the orbital basis set contains diffuse functions, as is the case for the aug-cc-pVXZ sets, the AutoAux fitting basis may contain (near-)linear dependencies. In this case, the Cholesky decomposition of the Coulomb metric will fail and the program will likely crash. One may print the offending auxiliary basis using `!PrintBasis` and manually remove the most diffuse s- and/or p-functions, which will usually resolve the problem. An alternative, automatic solution is also implemented – see section *Removal of Redundant Basis Functions*.

## 2.7.5 Effective Core Potentials

Starting from version 2.8.0, ORCA features effective core potentials (ECPs). They are a good alternative to scalar relativistic all-electron calculations if heavy elements are involved. This pertains to geometry optimizations and energy calculations but may not be true for property calculations.

In order to reduce the computational effort, the usually highly contracted and chemically inert core basis functions can be eliminated by employing ECPs. ECP calculations comprise a “valence-only” basis and thus are subject to the frozen core approximation. Contributions due to the core orbitals are accounted for by an effective one-electron operator  $U^{\text{core}}$  which replaces the interactions between core and valence electrons and accounts for the indistinguishability of the electrons. Its radial parts  $U_l(r)$  are generally expressed as a linear combination of Gaussian functions, while the angular dependence is included through angular momentum projectors  $|S_m^l\rangle$ .

$$U^{\text{core}} = U_L(r) + \sum_{l=0}^{L-1} \sum_{m=-l}^l |S_m^l\rangle [U_l(r) - U_L(r)] \langle S_m^l|$$

$$U_l = \sum_k d_{kl} r^{n_{kl}} \exp(-\alpha_{kl} r^2)$$

The maximum angular momentum  $L$  is generally defined as  $l_{\text{max}}^{\text{atom}} + 1$ . The parameters  $n_{kl}$ ,  $\alpha_{kl}$  and  $d_{kl}$  that are necessary to evaluate the ECP integrals have been published by various authors, among them the well-known Los Alamos (LANL) [41] and Stuttgart–Dresden (SD) [60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105] parameter sets. Depending on the specific parametrization of the ECP, relativistic effects can be included in a semiempirical fashion in an otherwise nonrelativistic calculation. Introducing  $U^{\text{core}}$  into the electronic Hamiltonian yields two types of ECP integrals, the local (or type-1) integrals that arise because of the maximum angular momentum potential  $U_L$  and the semi-local (or type-2) integrals that result from the projected potential terms. The evaluation of these integrals in ORCA proceeds according to the scheme published by Flores-Moreno et al.[106].

A selection of ECP parameters and associated basis sets is directly accessible in ORCA through the internal ECP library (see Table 2.38 for a listing of keywords).

Table 2.38: Overview of library keywords for ECPs and associated basis sets available in ORCA.

| ECP keyword          | Core size <sup>Page 83, 1</sup> | Elements    | Valence basis sets   |
|----------------------|---------------------------------|-------------|--|
| <i>Recommended</i>   |                                 |             |  |
| def-ECP              | 78                              | Fr–Ra       | Karlsruhe def2 basis sets:<br>def-SV(P), def-SVP, def-TZVP, def-TZVPP, ma-def-TZVP   |
| def2-ECP             | 60                              | Ac–Lr       | MINIX  |
|                      | 28                              | Rb–Xe       | Karlsruhe basis sets:<br>def2-SVP, def2-TZVP, etc.   |
|                      | 46                              | Cs–La       | def2-SVPD, def2-TZVPD, etc.  |
|                      | 28                              | Ce–Lu       | ma-def2-SVP, ma-def2-TZVP, etc.  |
| SK-MCDHF-RSC         | 60                              | Hf–Rn       | Correlation-consistent basis sets:<br>cc-pVnZ-PP, aug-cc-pVnZ-PP, cc-pCVnZ-PP, aug-cc-pCVnZ-PP, cc-pwCVnZ-PP, aug-cc-pwCVnZ-PP ( $n = \text{D, T, Q, 5}$ ) cc-pVnZ-PP ( $n = \text{D, T, Q}$ ) |
|                      | 10                              | Ca, Cu–Kr   |  |
|                      | 28                              | Sr–Xe       |  |
|                      | 46                              | Ba          |  |
|                      | 60                              | Hf–Rn       |  |
|                      | 78                              | Ra          |  |
| HayWadt <sup>2</sup> | 60                              | U           |  |
|                      | 10                              | Na–Cu       | LANL basis sets:<br>LANL2DZ, LANL2TZ, LANL2TZ(f), LANL08, LANL08(f)  |
|                      | 18                              | Zn          |  |
|                      | 28                              | Ga–Ag       |  |
|                      | 36                              | Cd          |  |
|                      | 46                              | In–La       |  |
|                      | 60                              | Hf–Au       |  |
|                      | 68                              | Hg–Tl       |  |
| dhf-ECP              | 78                              | Pb–Bi, U–Pu |  |
|                      | 28                              | Rb–Xe       | Karlsruhe dhf basis sets: dhf-SVP, dhf-TZVP, etc.  |
|                      | 46                              | Cs–Ba       |  |
|                      | 60                              | Hf–Rn, U    |  |
| vDZP-ECP             | 2                               | B–Mg        | vDZP   |
|                      | 10                              | Al–Zn       | uniquely compiled for the use with vDZP  |
|                      | 28                              | Ga–Cd       |  |

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