Auxiliary basis sets for main row atoms and transition metals and their use to approximate Coulomb potentials

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Abstract. We present auxilliary basis sets for the atoms H to At – excluding the Lanthanides – optimized for an efficient treatment of molecular electronic Coulomb interactions. For atoms beyond Kr our approach is based on effective core potentials to describe core electrons. The approximate representation of the electron density in terms of the auxilliary basis has virtually no effect on computed structures and affects the energy by less than 10^{-4} a.u. per atom. Efficiency is demonstrated in applications for molecules with up to 300 atoms and 2500 basis functions.

Key words: RI density functional theory – Fitting basis sets – Auxiliary basis sets

1 Introduction

Molecular electronic structure theory is essentially concerned with an accurate description of effects caused by the interelectronic repulsion. This is most easily demonstrated for density functional theory (DFT), which is based on a separation of two-electron contributions into a Coulomb and an exchange correlation term defined in terms of the electron density $\rho(\mathbf{r})$

$$J = \frac{1}{2} \int \rho(\mathbf{r}_1) \frac{1}{r_{12}} \rho(\mathbf{r}_2) \, d\tau, \tag{1}$$

$$E_{XC} = \int f(\rho, \nabla_\rho, \ldots) \, d\tau. \tag{2}$$

The conventional (exact) treatment of J in terms of two-electron four-centre integrals scales quadratically with molecular size for sufficiently large systems. The evaluation of E_{XC} typically requires a numerical integration

that has repeatedly been demonstrated – at least in principle – to scale linearly with the size of the system [1]. The relative effort required to treat J and E_{XC} depends, of course, on the actual implementation but timings reported for TURBOMOLE [2] are probably typical: E_{XC} requires more time than J for small molecules and already less than 10% (of J) for medium-sized cases (about 50 atoms, 500 basis functions).

The quest to extend the applicability of electronic structure treatments to larger and larger systems has led to intensive activities in developing efficient methods to deal with J. We only mention some very recent developments: linear scaling procedures to treat Coulomb, Eq. (1), [3, 4] and exchange terms [5], attenuated Coulomb operator techniques [6], and expansion of $\rho(\mathbf{r})$ in terms of an auxiliary (or fitting) basis, here denoted the RI-J ('resolution of the identity') approach

$$\rho(\mathbf{r}) \approx \tilde{\rho}(\mathbf{r}) = \sum_\alpha c_\alpha \alpha(\mathbf{r}) \ . \tag{3}$$

To avoid confusion we will denote the $\alpha(\mathbf{r})$ always as 'aux-basis' and employ the term 'basis' for the functions, denoted $v(\mathbf{r})$ or $\mu(\mathbf{r})$, used to represent molecular orbitals (MOs).

Details of the RI-J approach have been described in a recent article [2], and it has been demonstrated that careful optimization of the aux-basis leads to considerable gains in performance and only marginal sacrifices in accuracy as compared to the conventional technique based on four-centre integrals.

This work was based on and has been motivated by earlier work of Jan Almlöf and coworkers [7], which dealt with two important aspects of the RI-J technique:

1. It was shown that the appropriate metric to be used for the treatment of (3) should be based on the scalar product

$$(\rho_1|\rho_2) = \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d\tau \ . \tag{4}$$

2. It was demonstrated for the first time that errors resulting from the RI-J approximation could be made sufficiently small if this metric was used.

In this article we present aux-bases for the main row and transition metal elements H to At for use in connection with economic SVP[1] (split valence plus polarization) [8] and extended TZVP (triple zeta valence plus polarization) [9] basis sets. For the heavier atoms, beyond Kr, our work is based on effective core potentials (ECP). This approach is attractive since it is efficient and accounts for the most important relativistic effects.

The RI-J method also scales quadratically with system size but computational costs are reduced to less than 10% of a conventional treatment of J [2]. If the break-even point for conventional and linear scaling procedures occurs between 200 and 500 basis functions [4], it can be safely expected that the RI-J method is competitive at least for up to 2000 to 5000 basis functions. The methods presented in this work have a further advantage: they are available and proven for large systems.

2 Atomic basis sets and ECPs

For the atoms H–Kr we complement our previous work dealing with SVP bases and present aux-basis sets suited for TZVP bases. TZVP typically includes three Gaussian functions for each valence AO (atomic orbital) and a much more accurate representation of core AOs than SVP.

For main row and transition metal atoms beyond Kr we base our investigation on ECPs from the Stuttgart group [10]. The ECPs are of type 'mwb' (multielectron fit [11] to the quasirelativistic Wood-Boring total valence energies [12]) which includes relativistic corrections. The following core sizes have been selected:

Rb – Cd: ECP-28 (core $1s$-$3d$)
In – Ba: ECP-46 (core $1s$-$4d$)
Hf – Hg: ECP-60 (core $1s$-$4f$)
T1 – At: ECP-78 (core $1s$-$5d$)

With this choice we favour relatively small cores, since this appears necessary especially in DFT treatments [13]. However, the ECPs for In and T1 leave only three valence electrons and should be applied with great care since spurious effects cannot be excluded. To a lesser extent this warning also applies for the following elements Sn and Pb. For the basis sets to be used in connection with these ECPs we have essentially relied on the results of the Stuttgart group [10]. We have employed analytic gradient techniques to reoptimize orbital exponents and contraction coefficients by minimizing atomic SCF energies [8]. In the course of the basis set optimizations it appeared appropriate to modify most of the original basis sets – mainly designed to treat excited states of atoms – since a reduced number of primitive Gaussians and/or contractions turned out to be sufficient for molecular ground states. Despite the reduction in basis set size we have typically achieved a lowering of atomic SCF energies by a few mH (1 mH = 2.6 kJ/mol).

Our modifications concern mainly the transition metals. We propose two basis sets denoted SVP and TZVP which – for the sake of simplicity – are both derived from the very same set of primitive Gaussians and differ only in the contraction of the d functions, in the usual nomenclature,

Y – Cd: $(7s,6p,5d)$; SVP: $[5s,3p,2d]$, TZVP: $[5s,3p,3d]$
Hf – Hg: $(7s,6p,5d)$; SVP: $[6s,3p,2d]$, TZVP: $[6s,3p,3d]$.

The s functions include two (uncontracted) Gaussians describing the $5s$ and $6s$ AO, respectively. The most diffuse p function is of $5p$ and $6p$ type and thus a polarization function for the valence s AO.

3 Auxiliary basis sets

We have employed exactly the same techniques and fitting criteria to determine aux-bases as described in our previous work [2], and the reader is referred to this paper for details. The aux-bases are optimized as much as possible in atomic calculations, e.g. to determine their s, d and g parts. The p and f aux-basis functions have been optimized in representative molecular calculations. The basis set parameters obtained in this way served as a guide to fix the parameters for the remaining atoms. The design goals have also been taken from our previous work:

1. the error of J [resulting from the approximation, Eq. (3)] should be smaller than 0.02 mH in atomic calculations especially if the atomic density is not spherically symmetrical and includes d and g partial waves;
2. maximal errors of molecular Coulomb energies J should be 0.2 mH per atom at most. This threshold was chosen since the error in atomic SCF energies caused by even extended Gaussian basis set expansions is typically much larger than 1 mH.

3.1 Aux-bases for H–Kr

For designing aux-bases to be used in connection with TZVP bases sets, we have drawn on our experience with SVP basis sets. For the atoms beyond Ne it was found that the 'SVP aux-bases' fulfil the fitting criteria even for the TZVP basis and no appreciable improvement could be obtained by a reoptimization. This somewhat fortunate result demonstrates two important aspects: the SVP basis provides a reliable approximation of molecular densities $\rho(\mathbf{r})$, which is only slightly improved by TZVP treatments, and aux-bases are relatively insensitive with respect to details of $\rho(\mathbf{r})$.

For the first row atoms Li–Ne we had to extend the s part of the aux-basis (for TZVP as compared to SVP) to 9 primitives (instead of 8). The finally resulting aux-basis is characterized as:

Li–Ne, TZVP $(9s,3p,3d,1f)$ / $[7s,3p,3d,1f]$

This aux-basis can also be used in conjunction with an extended polarization basis such as $2d1f$ (added to TZV) without loss in accuracy.

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[1] If polarization functions on hydrogen atoms are deleted the basis set is referred to as SV(P)

3.2 Aux-bases for Rb–Cd, Cs, Ba, Hf–Hg

We propose a single aux-basis for each atom which can be used for SVP and TZVP basis sets. This simplification is well justified since SVP and TZVP are based on the same primitives and differ only in the contraction pattern. We typically arrive at the following:

aux-basis $(9s,4p,4d,3f,4g)/[7s,4p,3d,3f,2g]$.

Deviations from this specification mainly occur for alkali and alkaline earth metals. For Sr and Ba it is possible to reduce the polarizing functions to an uncontracted $(3p,3d,2f,1g)$ aux-basis; for Rb and Cs $(4p,4d)/[2p,2d]$ was found to be sufficient. The variation in the aux-basis size reflects the chemical behaviour of the elements. Rb and Cs form mainly ionic bonds, and if there are covalent contributions (Rb_2, etc.) they are dominated by valence s AOs, and either case is easy to describe. For Sr and Ba there are increased contributions of p and especially d AOs even in ionic compounds which require up to g functions in the aux-basis. Transition metals with an atomic occupation leading to a density $\rho(\mathbf{r})$ which is not spherically symmetrical require four g functions for a reliable description.

3.3 Aux-bases for In–Xe and Tl–At

For these elements only the valence s and p AOs are treated explicitly, the other electrons are incorporated in the core described by the ECP. Our work is in part preliminary, as mentioned above, since for In, Sn, Tl and Pb a smaller core appears preferable. As a consequence of the small number of valence electrons one also gets a small number of aux-basis functions, typically:

aux-basis $(5s,3p,3d,1f,1g)/[4s,3p,2d,1f,1g]$

3.4 Documentation

The aux-bases described here and in a previous paper (together with the corresponding basis sets to represent AOs) as well as the actual ECP parameters are available via FTP (file transfer protocol) at internet address "ftp.chemie.uni-karlsruhe.de" (internet number 129.13. 106.9) with login-ID "anonymous" in the directory "/pub/ri-j" or as supplementary material from the journal upon request.

For each atom we report the error in the atomic Coulomb energy J resulting from the approximate representation of $\rho(\mathrm{r})$, Eq. (3), as well as the error of J for at least one small molecule.

4 Accuracy: molecular energies and structure constants

In Table 1 we report errors caused by the RI-J approximation. This is done for the B-P parametrization [14] of the DFT in using grid m3 and m4 (which are explained below) for the quadrature. Since we consider an approximation of J, it is expected that neither the DFT parametrization nor the actual quadrature employed affects the results, as has been confirmed in test calculations.

The largest molecules of the test sample are shown in Figs. 1 and 2. The CdSe clusters are fractions of

Table 1. Accuracy ΔE (in mH) of computed total energies and maximum deviations of bond distances (Δr in pm) achieved with the pesent auxiliary basis sets in comparison to DFT results; all calculations have been performed using the B-P parametrization [14]. The following shorthand notation has been used: Ph = C_6H_5, en = $C_2H_4N_2$

Molecule/symmetry	Basis	Grid	ΔE	N_{atom}^a	Δr
Ag_4^+/D_{2h}	SVP	m3	0.288	4	0.0092
Sb_4/T_d	SVP	m3	0.251	4	0.0002
$I_2/D_{\infty h}$	SVP	m3	0.199	2	0.0195
IF_3/C_{2v}	SVP	m3	0.154	4	0.0045
Ta_2Cl_{10}/C_{2h}	SVP	m3	1.122	12	0.0052
OsO_4/T_d	SVP	m3	0.266	5	0.0022
$Hg_2Cl_2/D_{\infty h}$	SVP	m3	0.497	4	0.0874
$HgCl_2/D_{\infty h}$	SVP	m3	0.188	3	0.0066
$PbO/C_{\infty v}$	SVP	m3	0.109	2	0.0059
$PbO_2/D_{\infty h}$	SVP	m3	0.099	3	0.0399
$Pd(en)C_{11}H_{18}O_6)/C_1^b$	SVP	m3	4.514	48	–^{c}
$Pt(PPh_3)_3CO/C_3$	SV(P)^d	m3	3.040	105	0.0454
'$Cd_{32}Se_{50}$'/T^e	SV(P)	m4	5.306	134	–^{c}
'$Cd_{10}Se_{16}$'/T^f	SV(P)^g	m3	13.860	294	–^{c}
$C_2H_2/D_{\infty h}$	TZVP	m3	0.099	4	0.0181
C_6H_6/D_{6h}	TZVP	m3	0.724	12	0.0035
$NO/C_{\infty v}$	TZVP	m3	0.335	2	0.0056
$N_2/D_{\infty h}$	TZVP	m3	0.096	2	0.0010
$Cr(C_6H_6)_2/D_{6h}$	TZVP	m3	1.359	25	0.0058
$Hg_2Cl_2/D_{\infty h}$	TZVP	m3	0.575	4	0.0365

[a] Number of atoms
[b] Ref. [21]
[c] No conventional DFT structure optimization performed
[d] SV bases for Ph ligands and SVP for the remaining atoms
[e] $Cd_{32}Se_{14}(SeH)_{36}(PH_3)_4$, Ref. [15], See Fig. 1
[f] $Cd_{10}Se_4(SePh)_{12}(PPh_3)_4$, Ref. [15], See Fig. 2
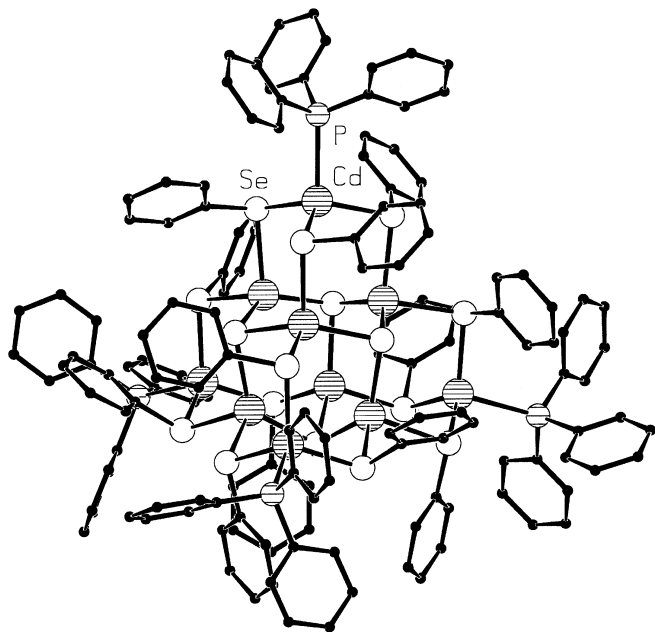[g] Ph ligands decribed by single zeta (SZ) bases as explained in the text

Fig. 1. Computed structure of $Cd_{10}Se_4(SePh)_{12}(PPh_3)_4$ [15] in T symmetry; H atoms are not shown

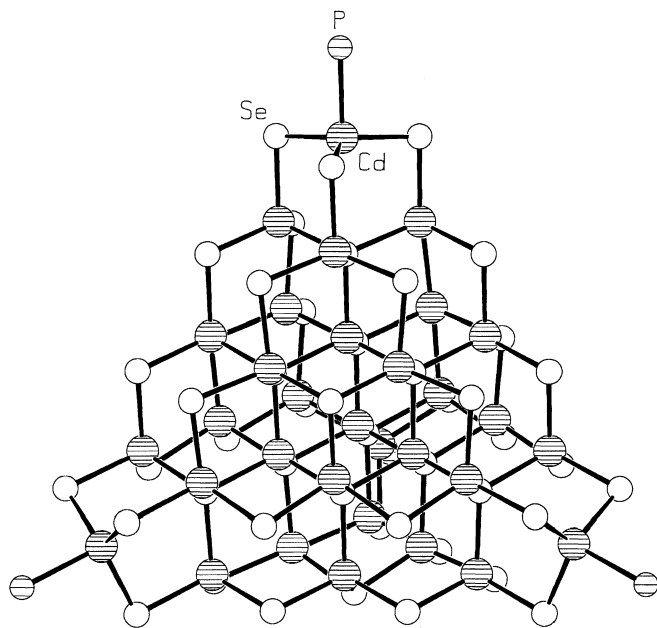**Fig. 2.** Computed structure of $Cd_{32}Se_{14}(SeH)_{36}(PH_3)_4$ [15] in T symmetry, H atoms are not shown

sphalerite crystal structure with a cluster core $Cd_{10}Se_{16}$ and $Cd_{32}Se_{50}$, respectively. The compounds are known experimentally [15]; the dangling bonds of Se are saturated by phenyl groups as in Fig. 1. For the larger cluster, Fig. 2, we have replaced the phenyl groups by hydrogen atoms.

Errors in computed DFT energies are typically below 0.1 mH per atom, much like in our previous work for SVP bases for H–Kr. The largest error in [2] occurred for the molecule NO with 0.3 mH per atom, second line of

Table 1 in [2]. This was actually a mistake on our part: the error is only 0.14 mH per atom.

The errors ΔJ resulting from the RI-J approximation always have the same sign and thus largely cancel for computed reaction energies. In our judgement even an error of 0.1 mH per atom is of little consequence, since it is at least an order of magnitude smaller than errors introduced by the basis set employed to represent MOs and especially the errors owing to the DFT.

For the largest molecule included in Table 1, $Cd_{10}Se_4(SePh)_{12}(PPh_3)_4$ with 294 atoms, even the total error in the energy resulting from the RI-J approximation is only 14 mH (less than 9 kcal/mol or 40 kJ/mol): a corresponding accuracy presently appears out of reach of any experimental technique.

The deviations in computed bond distances are typically below 0.1 pm and therefore almost meaningless (this error is already within the scatter of the relaxation procedure employed to determine equilibrium structures).

5 Representative timings

The present code differs in some details from the one described previously [2]:

1. Integral routines have been extended to the treatment of functions with higher l quantum numbers: up to g functions (l = 4) in the basis set and up to i (l = 6) functions in the aux-basis.
2. Special routines for three-centre integrals $(v\mu|\alpha)$ have been included for s and p functions, e.g. $(ss|s)$ up to $(pp|p)$ and $(ds|p)$.
3. In the quadrature we employ multi-grids proposed by Tozer et al. [16]. Based on our previous grids with size 1 (coarse) to 5 (fine) we now use the multigrids m3 to m5: in the SCF iterations grids 1–3 are applied, the final energy and the gradient are evaluated with grids 3–5 (an upgrade by two stages in grid size). We recommend grid m3 for smaller molecules, less than 50 atoms, and grid m4 for larger molecules. The multi-grid feature reduces costs for the quadrature to less than 30% without loss in accuracy.
4. Fine-tuning in the prescreening techniques to avoid the accumulation of negligible contributions – integrals and quadrature – have also increased efficiency [17].
5. The construction of the inverse of $(\alpha|\beta)$ is now avoided, the system of linear equations necessary for the RI-J technique, Eq. (7) of [2], is now solved directly by the Cholesky decomposition of $(\alpha|\beta)$ [18].
6. Memory requirements have been reduced by more careful dynamic storage allocations.

In Table 2 we pesent timings obtained with the present code, TURBOMOLE 4.0. All molecules considered show three-dimensional space filling. We have not included 'one-dimensional' model systems, which would lead to considerably better timings for the quadrature and the evaluation of J. For a better comparison

Table 2. Timings, in seconds for an HP J210 workstation, for the dominant steps in an SCF-DFT calculation for selected molecules from Table 1

Molecule/symmetry	N_{BF}^a	N_J^b	Memory[c]	t_{prep}^d	t_{RI-J}^e/type[f]	t_{quad}^g/grid	t_J^h
Pd(en)($C_{11}H_{18}O_6$)/C_1	448	1053	9	15.62	195.22/d	226.94 /m3	2227.64
			269	81.50	83.93/sd		
			646	129.19	11.08/i		
Pt $(PPh_3)_3CO$/C_3	682	2490	7	14.80	433.18/d	260.91/m3	4216.90
			251	117.11	257.62/sd		
			687	206.15	114.79/sd		
'$Cd_{10}Se_{16}$'/T	1880	6032	16	10.36	1084.75/d	296.07/m3	14030.96
						596.02/m4	
			277	132.59	874.93/sd		
			634	271.01	640.38/sd		
'$Cd_{32}Se_{50}$'/T	2536	4776	28	7.30	1154.08/d	749.15/m4	17889.87
			253	113.07	964.33/sd		
			610	206.19	807.96/sd		

[a] Number of orbital basis functions
[b] Number of auxiliary basis functions
[c] Core memory allocated for RI-J arrays in MB
[d] Time for computation of in-core arrays $(\nu\mu|\alpha)$, $(\alpha|\beta)$, and decomposition of $(\alpha|\beta)$
[e] Time per iteration for the calculation of the RI-J coulomb part
[f] In-core (i), semi-direct (sd) or direct (d) treatment of the RI-J coulomb part
[g] Time for the calculation of E_{XC} and the grid used
[h] Time for the conventional calculation of the coulomb terms (first SCF iteration)

Table 3. Timings, in minutes for an HP J210 workstation, for complete energy and gradient calculations for selected molecules from Table 1

Molecule/symmetry	Memory[a]	N_{iter}^b	$t_{RI\ energy}^c$	$t_{RI\ grad}^d$	$t_{DFT\ energy}^e$	$t_{DFT\ grad}^f$
Pd (en)($C_{11}H_{18}O_6$)/C_1	646	17[g]	99	31	480	83
Pt($PPh_3)_3CO$/C_3	688	19[g]	167	58	998	127
'$Cd_{10}Se_{16}$'/T	732	11[h]	230	98	–	–
'$Cd_{32}Se_{50}$'/T	610	9[h]	290	125	–	–

[a] Core memory in MB for the RI-J energy calculation
[b] Number of iterations needed for convergence
[c] Time for the complete RI-J energy calculation
[d] Time for the complete RI-J gradient calculation
[e] Time for the complete conventional DFT energy calculation
[f] Time for the conventional DFT gradient calculation
[g] Extended Hückel guess
[h] Typical structure optimization cycle

of timings we further note that using grid m4 is roughly twice as costly as using grid m3.

On our HP J210 workstation (HP PA RISC 7200)[2], equipped with 1 GB main memory, we can easily store the three-centre integrals $(\nu\mu|\alpha)$ for up to 500 basis functions in C_1 symmetry, case 1 in Table 2, and up to about 2000 basis functions in O_h symmetry. In this in-core mode, costs for RI-J are just 0.5% of that for a conventional treatment of J, and the quadrature remains as the only demanding part of the calculation.

In the direct mode – the $(\nu\mu|\alpha)$ are computed twice in each iteration unless their contribution is negligible [2] – costs for quadrature and RI-J are comparable only for the smallest molecule, case 1, but the RI-J part slightly dominates for the larger cases. This reflects the different scaling behaviour: costs scale asymptotically as N^2 for RI-J and increase like $N^{1.5}$ for the quadrature implemented in TURBOMOLE. The picture would be different without the multi-grid feature since costs for the

quadrature would increase by a factor of three and this step would normally dominate. In any case it can be seen that even RI-J in direct mode is at least 10 times faster than the conventional evaluation of coulomb terms.

In the semi-direct mode we store the most costly integrals in memory and recompute only the remaining ones in each iteration. For all cases in Table 2 in which we allocate $\approx$650 MB we gain at least a factor of 22 as compared to a conventional treatment of J.

The third example in Table 2 is somewhat special since we have used a highly contracted basis set for the phenyl group. This was derived from a fully molecule optimized basis for benzene [8], characterized as $(7s,4p)$/$[3s,1p]$ for C and $(4s)$/$[1s]$ for H. Despite the contraction to almost single zeta, this basis gives a reliable description of bonding, structure and steric requirements. For the phenyl group we use this basis for all except the link atom where an SV basis is used. This procedure leads to a relatively small number of basis functions and a large number of aux-basis functions.

The timings presented in Table 2 can be considered as worst case since we have always employed the full aux-basis described in the present work. This is a conservative procedure since reduced aux-bases obtained by

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deleting f and/or g functions will suffice in many cases at least for structure determinations [2, 19, 20].

Table 3 finally gives the total CPU time needed for complete RI-J energy and gradient calculations in comparison with a conventional run. For energy calculations we gain at least a factor 5 to 6, and the gradient is up to 3 times faster than in a conventional treatment. For a whole cycle of a structure optimization this means an effective acceleration of a factor 4 to 5 in the examples given.

A typical geometry optimization iteration cycle (energy plus gradient) for $Cd_{10}Se_4(SePh)_{12}(PPh_3)_4$, Fig. 1, with 294 atoms, or $Cd_{32}Se_{14}(SeH)_{36}(PH_3)_4$, Fig. 2, with 2536 basis functions requires about 7 h on a workstation in the relatively low symmetry T. This makes structure optimizations possible.

6 Summary

We have presented accuracies and timings which demonstrate that the RI-J method allows for the treatment of molecules with up to 300 atoms and/or 2500 basis functions in moderate symmetry (D_{2h} or T) on work stations. The sample molecules considered in the present work are not model cases: all systems treated were brought to our attention since there were problems with experiments, and geometry optimizations have been carried out in all cases. The methodology presented is proven for molecules involving main row elements and transition metals – only Lanthanides and Actinides are not covered in this work. The aux-bases described in the present article together with the RI-J method have further been shown to be valuable for the treatment of electronic excitations within DFT methods [17]. The gains in efficiency and the accuracy achieved by using the RI-J method are comparable to the results presented here, and allow for the first time the treatment of electronic excitations for systems of the size considered in this work.

The efficiency of the RI-J technique can still be considerably improved. For large molecules one has to use the direct mode and the computation of $(v\mu|\alpha)$ becomes the dominant step. If the differential overlap between $v(\mathbf{r})\mu(\mathbf{r})$ and $\alpha(\mathbf{r})$ is sufficiently small, one can replace $\alpha(\mathbf{r})$ by a point charge if α is an s function, a

point dipole if α is a p function, etc. These cases still scale quadratically with system size but the evaluation is less costly. Explicit evaluation of $(v\mu|\alpha)$ is thus only required for overlapping $v(\mathbf{r})\mu(\mathbf{r})$ and $\alpha(\mathbf{r})$, which scale linearly with molecular size.

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