
Analytical Evaluation of Pseudopotential Matrix Elements with Gaussian-Type Solid Harmonics of Arbitrary Angular Momentum

ANGUANG HU, MARKUS STAUFER, UWE BIRKENHEUER,
VALENTIN IGOSHINE, NOTKER RÖSCH

Fachgebiet für Theoretische Chemie, Technische Universität München, 85747 Garching, Germany

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ABSTRACT: An efficient formalism for evaluating pseudopotential matrix elements with Gaussian-type solid harmonics of arbitrary angular momentum is presented. It is based on the tensor coupling technique, which is especially well suited for treating Gaussian-type solid harmonics of arbitrary angular momentum. Closed analytical expressions are derived for the matrix elements as well as for their nuclear displacement derivatives. The efficiency of the implementation into our new parallel density functional program PARAGAUSS and the quality of the pseudopotential approach is tested for a set of representative molecules and cluster models. To this end the results of pseudopotential calculations are compared to those of nonrelativistic and scalar-relativistic all-electron calculations. © 2000 John Wiley & Sons, Inc. *Int J Quantum Chem* 79: 209–221, 2000

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Introduction

In many problems of atomic and molecular physics the electrons of a system can be separated into valence and core electrons. Very often the important physical properties are determined by the valence electrons only. One of the first examples

considered were atomic spectra. Pseudopotentials had been developed to deal with atoms by essentially restricting the treatment to the valence electrons [1]. Nowadays, pseudopotentials have matured to an important tool in computational physics and chemistry. Due to the presence of the pseudopotentials, only nodeless pseudovalence orbitals have to be taken into account when solving the effective one-particle equations. That directly implies that in a basis-set-driven formalism—as most of the commonly applied methods are—much smaller basis

Correspondence to: N. Rösch.

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sets are sufficient than in standard all-electron calculations.

Moreover, when modeling fully ionic substrates by finite clusters, atomic centers that carry pseudopotentials (or model potentials), but no basis functions are preferable to bare point-charge arrays when embedding the cluster models. In this way artificial distortions of the electron density at the cluster boundary due to the point charges can be avoided [2–6].

From a technical point of view usage of pseudopotentials requires the evaluation of additional types of multicenter integrals. Of course, it is highly desirable that matrix elements involving pseudopotentials can be evaluated along a similar line as those integrals that have to be evaluated anyhow in density functional or conventional quantum chemistry codes. Most ab initio quantum chemistry programs use Gaussian-type basis functions (Gaussians) because they permit an analytical evaluation of pertinent integrals. Thus, it is an obvious move to also represent pseudopotentials by Gaussians.

For Cartesian Gaussians the method of evaluating pseudopotentials is well established [7, 8]. However, when considering higher angular momenta, it is beneficial to switch from Cartesian Gaussians [9, 10] to Gaussian-type solid harmonics (or spherical Gaussians) [11, 12] which are defined as

$$\chi_m^{la\alpha}(\mathbf{r}) = N(l, \alpha) \mathcal{Y}_m^l(\mathbf{r} - \mathbf{a}) \exp[-\alpha(\mathbf{r} - \mathbf{a})^2] \quad (1)$$

with

$$\mathcal{Y}_m^l(r, \theta, \phi) = \sqrt{\frac{4\pi}{2l+1}} r^l Y_{lm}(\theta, \phi) \quad (2)$$

and

$$N(l, \alpha) = \left(\frac{2\alpha}{\pi}\right)^{3/4} \left[\frac{(4\alpha)^l}{(2l-1)!!}\right]^{1/2}. \quad (3)$$

Here $Y_{lm}(\theta, \phi)$ are spherical harmonics with the phase conventions of Condon and Shortley [13–15], and $\mathcal{Y}_m^l(\mathbf{r})$ denote the corresponding harmonic polynomials. To emphasize the difference, the latter will be referred to in the following as “solid harmonics.” For the sake of simplicity, we stick to complex solid harmonics in this presentation. Generalization to real solid harmonics is straightforward (see discussion of real solid harmonics).

Gaussian-type solid harmonics offer several advantages. First, for an angular momentum $l > 1$ there exist fewer functions than there are Cartesian Gaussians. Second, at variance with Cartesian Gaussians/Hermite Gaussians, Gaussian-type solid harmonics exhibit the same angular dependence in both real and momentum space, which

is much more convenient when Fourier transformations are desired, e.g., when applying periodic boundary conditions in band structure calculations. Third, and most importantly, Gaussian-type solid harmonics permit an easy way for deriving matrix elements of functions of higher angular momentum, once the analytical form of the matrix elements of s -type functions is known. Using the theorem of Hobson [16],

$$\mathcal{Y}_m^l(\nabla_r)f(r) = 2^l \mathcal{Y}_m^l(\mathbf{r}) \left(\frac{\partial}{\partial r^2}\right)^l f(r), \quad (4)$$

the basis functions of higher angular momentum can be written as nuclear displacement derivatives of the corresponding s -type functions [17]:

$$\chi_m^{la\alpha}(\mathbf{r}) = N(l, \alpha) \left(\frac{1}{2\alpha}\right)^l \mathcal{Y}_m^l(\nabla_a) \exp[-\alpha(\mathbf{r} - \mathbf{a})^2]. \quad (5)$$

This essentially reduces the analytical evaluation of matrix elements with basis functions of higher angular momentum to performing nuclear displacement derivatives. The resulting algorithm requires an effort comparable to the recursion relations of Cartesian Gaussians [10]. Reducing the matrix element evaluation to nuclear displacement derivatives is also feasible for Hermite Gaussians. However, the required product and differentiation rules, which read

$$\mathcal{Y}_m^l(\nabla)[f(\mathbf{r})g(\mathbf{r})] = \sum_{l'=0}^l \sum_{m'} \varepsilon_{ll'mm'} [\mathcal{Y}_{m'}^{l'}(\nabla)f(\mathbf{r})] \times [\mathcal{Y}_{m-m'}^{l-l'}(\nabla)g(\mathbf{r})] \quad (6)$$

and

$$\mathcal{Y}_{-m'}^{l'}(\nabla)\mathcal{Y}_m^l(\mathbf{r}) = (-1)^{m'} (2l' - 1)!! \varepsilon_{ll'mm'} \mathcal{Y}_{m-m'}^{l-l'}(\mathbf{r}) \quad (7)$$

in case of Gaussian-type solid harmonics, become much more complicated for Hermite Gaussians [17]. The ε coefficients, which are the same for both relations, are generally expressed [17] in terms of Clebsch–Gordan coefficients [15]. We were able to find a simple close expression for these coefficients:

$$\varepsilon_{ll'mm'} = \sqrt{\binom{l+m}{l'+m'} \binom{l-m}{l'-m'}}. \quad (8)$$

An analytical method for evaluating pseudopotential matrix elements with Cartesian Gaussians has previously been proposed [18]. It is based on a technique originally introduced by Löwdin [19]. Many improvements have been suggested in the meantime, e.g., new recursion relations and alternative approaches to fundamental integrals [20]

or techniques based on numerical quadrature [21]. However, the number of floating-point operations required in all these algorithms is still rather high, especially when basis functions of higher angular momentum are considered. The tensor coupling strategy, i.e., application of Eqs. (6) and (7), for Gaussian-type solid harmonics [17] is much more promising here. It is applied throughout our whole new parallel quantum chemistry program PARAGAUSS [22, 23]. In principle, the tensor coupling technique exists in two variants, a vector-coupled form and an uncoupled form [17]. In line with earlier observations on standard matrix elements [17], we found that also in the case of pseudopotential matrix elements the uncoupled form is significantly more efficient (less number of required floating-point operations) than the vector-coupled form. We therefore restrict our presentation to the uncoupled formalism.

In this study, we present an efficient way to evaluate pseudopotential matrix elements with Gaussian-type solid harmonics of arbitrary angular momentum by combining the method already developed for Cartesian Gaussians [7] with the tensor coupling technique for Gaussian-type solid harmonics. Closed analytical expressions will be given based on well-known integrals over products of modified spherical Bessel functions i_l and algebraic and/or exponential functions, the so-called Q integrals [24]:

$$Q_l^n(k, \eta) = \int_0^\infty i_l(kr)r^n \exp(-\eta r^2) dr \quad (9)$$

and

$$Q_{l_1 l_2}^n(k_1, k_2; \eta) = \int_0^\infty i_{l_1}(k_1 r) i_{l_2}(k_2 r) r^n \exp(-\eta r^2) dr. \quad (10)$$

Actually, these Q integrals are the same as the ones used to evaluate pseudopotential matrix elements with Cartesian Gaussians [7, 8]. Their numerical evaluation has been described in detail in Ref. [24]. Furthermore, it is demonstrated that evaluating the pseudopotential matrix elements by the tensor coupling technique allows a straightforward extension of the formulas to analytical derivatives of the matrix elements with respect to the nuclear positions.

The literature on the use of pseudopotentials is large [25, 26]. We only mention recent investigations exploring the use of Hartree–Fock derived pseudopotentials in the context of density functional methods [27, 28], some alternative algorithms for evaluating pertinent integrals [20, 21], and the

implementation of second-order integral derivatives [29, 30].

Evaluation of the Pseudopotential Matrix Elements

BASIC MATRIX ELEMENTS

When applying pseudopotential techniques, the potential of an atom located at position \mathbf{c} is generally written as

$$V(\mathbf{r}) = -\frac{Z}{|\mathbf{r} - \mathbf{c}|} + V_P(\mathbf{r} - \mathbf{c}), \quad (11)$$

where Z is nuclear charge of the atom and $V_P(\mathbf{r} - \mathbf{c})$ the so-called pseudopotential. Almost all pseudopotentials used in quantum chemistry [31–37] are of the general form [38]

$$V_P(\mathbf{r} - \mathbf{c}) = \frac{Z_{\text{core}}}{r_c} + V^{\text{loc}}(r_c) + \sum_{l=0}^L \sum_m |Y_{lm}(\Omega_c)\rangle V^l(r_c) \langle Y_{lm}(\Omega_c)| \quad (12)$$

with $r_c = |\mathbf{r} - \mathbf{c}|$ and $\Omega_c = (\mathbf{r} - \mathbf{c})/r_c$. Here, Z_{core} is the charge of the atomic core and L is the highest angular momentum occurring among the core electrons. Smoothed electrostatic contributions of the core electrons such as $\text{erf}(\eta r_c)/r_c$ are not considered here. They can be treated on the same footing as a standard unscreened Coulomb potential Q/r_c . In Eq. (12) $Y_{lm}(\Omega_c)$ are spherical harmonics centered at location \mathbf{c} , and $\langle Y_{lm}(\Omega_c)|$ implies a projection onto the angular dependence of the spherical harmonics, i.e.,

$$\langle Y_{lm}(\Omega_c)| f(r_c, \Omega_c) \rangle = \int Y_{lm}^*(\Omega_c) f(r_c, \Omega_c) d\Omega_c \quad (13)$$

is still a function of r_c . This representation of pseudopotentials results in two new types of integrals:

$$V_{\text{abc}\alpha\beta}(l_a, m_a; l_b, m_b) = \langle \chi_{m_a}^{l_a \alpha} | V^{\text{loc}}(r_c) | \chi_{m_b}^{l_b \beta} \rangle \quad (14)$$

and

$$W_{\text{abc}\alpha\beta}^l(l_a, m_a; l_b, m_b) = \sum_m \int_0^\infty \langle \chi_{m_a}^{l_a \alpha} | Y_{lm}(\Omega_c) \rangle \times V^l(r_c) \langle Y_{lm}(\Omega_c) | \chi_{m_b}^{l_b \beta} \rangle r_c^2 dr_c. \quad (15)$$

For computational convenience the radial potentials V^{loc} and V^l are usually fitted to Gaussian-type

functions [38]:

$$V^x(r) = \frac{1}{r^2} \sum_j d_j^x r^{n_j^x} \exp(-\gamma_j^x r^2),$$

for $x = \text{loc}, 0, 1, \dots$, (16)

where d_j^x and γ_j^x represent the coefficients and Gaussian exponents, respectively, for the parameterization of the pseudopotential; n_j^x are integers ranging from 0 to 2. This form is even used for pseudopotentials that originally were generated numerically, e.g., [39, 40]. Thus Eqs. (14) and (15) reduce to

$$V_{\text{abc}\alpha\beta}(l_a, m_a; l_b, m_b) = \sum_j d_j^{\text{loc}} V_{\text{abc}\alpha\beta\gamma_j^{\text{loc}}}^{n_j^{\text{loc}}}(l_a, m_a; l_b, m_b),$$

(17)

with

$$V_{\text{abc}\alpha\beta\gamma}^{n_j}(l_a, m_a; l_b, m_b) = \langle \chi_{m_a}^{l_a a\alpha} | r_c^{n_j-2} \exp(-\gamma r_c^2) | \chi_{m_b}^{l_b b\beta} \rangle$$

(18)

and

$$W_{\text{abc}\alpha\beta}^l(l_a, m_a; l_b, m_b) = \sum_j d_j^l W_{\text{abc}\alpha\beta\gamma_j^l}^{l_j}(l_a, m_a; l_b, m_b)$$

(19)

with

$$W_{\text{abc}\alpha\beta\gamma}^{l_j}(l_a, m_a; l_b, m_b) = \sum_m \int_0^\infty \langle \chi_{m_a}^{l_a a\alpha} | Y_{lm}(\Omega_c) \rangle \times r_c^{n_j} \exp(-\gamma r_c^2) \langle Y_{lm}(\Omega_c) | \chi_{m_b}^{l_b b\beta} \rangle dr_c.$$

(20)

EVALUATION OF V-TYPE MATRIX ELEMENTS

First consider the matrix elements $V_{\text{abc}\alpha\beta\gamma}^{n_j}(l_a, m_a; l_b, m_b)$, Eq. (18). As outlined in the Introduction, evaluation of such matrix elements begins by deriving an analytical expression for s -type orbital functions on both sides, i.e.,

$$V_{\text{abc}\alpha\beta\gamma}^{n_j}(0, 0; 0, 0) = \langle \chi_0^{0a\alpha} | r_c^{n_j-2} \exp(-\gamma r_c^2) | \chi_0^{0b\beta} \rangle.$$

(21)

Using Eq. (1) and $\mathcal{Y}_0^0(\mathbf{r}) = 1$, they read

$$V_{\text{abc}\alpha\beta\gamma}^{n_j}(0, 0; 0, 0) = N(0, \alpha)N(0, \beta) \times \int \exp[-\alpha(\mathbf{r} - \mathbf{a})^2] \exp[-\beta(\mathbf{r} - \mathbf{b})^2] \times \exp[-\gamma(\mathbf{r} - \mathbf{c})^2] |\mathbf{r} - \mathbf{c}|^{n_j-2} d^3r.$$

(22)

The evaluation of these integrals proceeds by re-expanding the exponentials $\exp[-\alpha(\mathbf{r} - \mathbf{a})^2]$ and $\exp[-\beta(\mathbf{r} - \mathbf{b})^2]$ around center \mathbf{c} according to

$$\exp[-\alpha(\mathbf{r} - \mathbf{a})^2] = \exp[-\alpha(\mathbf{r} - \mathbf{c})^2] \times \exp[+2\alpha(\mathbf{a} - \mathbf{c})(\mathbf{r} - \mathbf{c})] \exp[-\alpha(\mathbf{a} - \mathbf{c})^2].$$

(23)

Introducing the short-hand notations

$$D = \exp[-\alpha(\mathbf{a} - \mathbf{c})^2] \exp[-\beta(\mathbf{b} - \mathbf{c})^2],$$

(24)

$$\mathbf{k} = 2\alpha(\mathbf{a} - \mathbf{c}) + 2\beta(\mathbf{b} - \mathbf{c}),$$

(25)

$$\eta = \alpha + \beta + \gamma$$

(26)

one obtains

$$V_{\text{abc}\alpha\beta\gamma}^{n_j}(0, 0; 0, 0) = N(0, \alpha)N(0, \beta)D \times \int \exp[\mathbf{k}(\mathbf{r} - \mathbf{c})] |\mathbf{r} - \mathbf{c}|^{n_j-2} \times \exp[-\eta(\mathbf{r} - \mathbf{c})^2] d^3r.$$

(27)

Switching to polar coordinates around center \mathbf{c} , using the well-known expansion [41]

$$\exp(\mathbf{k}\mathbf{r}) = 4\pi \sum_{l=0}^{\infty} \sum_m i_l(kr) Y_{lm}^*(\Omega_r) Y_{lm}(\Omega_k)$$

(28)

with $\Omega_r = \mathbf{r}/r$ and $\Omega_k = \mathbf{k}/k$, and invoking the orthonormality of spherical harmonics, the s -type matrix elements reduce to

$$V_{\text{abc}\alpha\beta\gamma}^{n_j}(0, 0; 0, 0) = N(0, \alpha)N(0, \beta)4\pi D Q_0^n(k, \eta),$$

(29)

where

$$Q_0^n(k, \eta) = \int_0^\infty i_0(kr) r^n \exp(-\eta r^2) dr$$

(30)

is the $l = 0$ version of the one-index Q integral defined in Eq. (9). Note that here k denotes $|\mathbf{k}|$. Thus, as expected, the s -type matrix elements $V_{\text{abc}\alpha\beta\gamma}^{n_j}(0, 0; 0, 0)$ do not depend on the relative orientation of the three centers \mathbf{a} , \mathbf{b} , and \mathbf{c} in space.

Having reached our first goal, an analytical expression for the s -type matrix elements, we now turn to the evaluation of the matrix elements for basis functions of arbitrary angular momentum. We start from Eq. (5), which expresses the non- s -type orbital basis functions $\chi_m^{l_a a\alpha}(\mathbf{r})$ as nuclear displacement derivatives. Inserting these expressions into the defining equation [Eq. (18)] and using the final form of the s -type matrix elements [Eq. (29)] yields

$$V_{\text{abc}\alpha\beta\gamma}^{n_j}(l_a, m_a; l_b, m_b) = \frac{N(l_a, \alpha)N(l_b, \beta)}{(2\alpha)^{l_a}(2\beta)^{l_b}} \mathcal{Y}_{m_a}^{l_a}(\nabla_a) \times \mathcal{Y}_{m_b}^{l_b}(\nabla_b) [4\pi D Q_0^n(k, \eta)].$$

(31)

These derivatives are evaluated by multiple application of the product rule [Eq. (6)], the differentiation rule [Eq. (7)], and the theorem of Hobson [Eq. (4)]. In addition, the following relation between one-index Q integrals is used:

$$\mathcal{Y}_m^l(\nabla_k) [Q_{l'}^{n+l'}(k, \eta)/k^{l'}] = \mathcal{Y}_m^l(\mathbf{k}) Q_{l+l'}^{n+l+l'}(k, \eta)/k^{l+l'}.$$

(32)

Applying the theorem of Hobson, this relation follows immediately from the generalized upward recursion for modified spherical Bessel functions $i_n(x)$ [41]:

$$\left(\frac{1}{x} \frac{d}{dx}\right)^m \frac{i_n(x)}{x^n} = \frac{i_{n+m}(x)}{x^{n+m}}. \quad (33)$$

In summary, the final formula for V -type matrix elements with basis functions of arbitrary angular momentum is

$$\begin{aligned} V_{\text{abca}\beta\gamma}^n(l_a, m_a; l_b, m_b) &= N(l_a, \alpha)N(l_b, \beta)D \\ &\times \sum_{l_1=0}^{l_a} \sum_{m_1} \varepsilon_{l_a l_1 m_a m_1} \mathcal{Y}_{m_a - m_1}^{l_a - l_1}(\mathbf{c} - \mathbf{a}) \\ &\times \sum_{l_2=0}^{l_b} \sum_{m_2} \varepsilon_{l_b l_2 m_b m_2} \mathcal{Y}_{m_b - m_2}^{l_b - l_2}(\mathbf{c} - \mathbf{b}) \\ &\times \sum_{\lambda} (2\lambda - 1)!! Q_{l_1 + l_2 - \lambda}^{n + l_1 + l_2 - \lambda}(k, \eta) / k^{l_1 + l_2 - \lambda} \\ &\times \sum_{\mu} (-1)^{\mu} \varepsilon_{l_1 \lambda m_1 \mu} \varepsilon_{l_2 \lambda m_2, -\mu} \mathcal{Y}_{m_1 - \mu}^{l_1 - \lambda}(\mathbf{k}) \\ &\times \mathcal{Y}_{m_2 + \mu}^{l_2 - \lambda}(\mathbf{k}). \end{aligned} \quad (34)$$

Equation (34) features 10 independent angular indices, the running indices l_a, m_a, l_b, m_b , and the summation indices $l_1, m_1, l_2, m_2, \lambda$, and μ . However, it is possible to factorize the expression such that at most seven angular indices have to be treated simultaneously. This factorization is indicated by the order of the summation symbols in Eq. (34).

Special care has to be taken in case the auxiliary vector k becomes zero, i.e., in case the effective center $(\alpha \mathbf{a} + \beta \mathbf{b}) / (\alpha + \beta)$ of the two basis functions $\chi_{m_a}^{l_a \alpha}$ and $\chi_{m_b}^{l_b \beta}$ coincides with the center \mathbf{c} of the pseudopotential. From the asymptotic behavior of the modified spherical Bessel functions [41],

$$i_l(x) \stackrel{x \rightarrow 0}{\approx} \frac{x^l}{(2l+1)!!}, \quad (35)$$

it follows that

$$Q_l^n(k, \eta) \stackrel{k \rightarrow 0}{\approx} \frac{k^l}{(2l+1)!!} \int_0^{\infty} r^{n+l} \exp(-\eta r^2) dr. \quad (36)$$

Thus the limiting case $k \rightarrow 0$ in $Q_l^n(k, \eta) / k^l$ does not cause serious problems.

EVALUATION OF W -TYPE MATRIX ELEMENTS

We now turn to the second type of matrix elements, the W -type matrix elements. As evident from Eqs. (15) or (20), one first has to find the projection

integrals

$$\begin{aligned} P_{\text{ac}\alpha}^{lm}(l_a, m_a; r_c) &= \langle Y_{lm}(\Omega_c) | \chi_{m_a}^{l_a \alpha} \rangle \\ &= \int Y_{lm}^*(\Omega_c) \chi_{m_a}^{l_a \alpha}(\mathbf{r}) d\Omega_c. \end{aligned} \quad (37)$$

Their evaluation is very similar to that of V -type matrix elements discussed in the previous section. Re-expressing the exponential $\exp[-\alpha(\mathbf{r} - \mathbf{a})^2]$ around center \mathbf{c} [Eq. (23)], switching to polar coordinates of \mathbf{c} , and using the expansion of $\exp(\mathbf{k}\mathbf{r})$ in spherical harmonics [Eq. (28)], the s -type variant of the projection integrals becomes

$$\begin{aligned} P_{\text{ac}\alpha}^{lm}(0, 0; r_c) &= N(0, \alpha) \exp[-\alpha(\mathbf{a} - \mathbf{c})^2], \\ &\times 4\pi i_l(k_a r_c) Y_{lm}(\Omega_{k_a}) \end{aligned} \quad (38)$$

with

$$\begin{aligned} \mathbf{k}_a &= 2\alpha(\mathbf{a} - \mathbf{c}), & k_a &= |\mathbf{k}_a|, \\ \Omega_{k_a} &= \mathbf{k}_a / k_a. \end{aligned} \quad (39)$$

Equation (38) may be reexpressed in terms of solid harmonics:

$$\begin{aligned} P_{\text{ac}\alpha}^{lm}(0, 0; r_c) &= N(0, \alpha) \sqrt{4\pi(2l+1)} \exp[-\alpha(\mathbf{a} - \mathbf{c})^2] \\ &\times i_l(k_a r_c) / k_a^l \mathcal{Y}_m^l(\mathbf{k}_a). \end{aligned} \quad (40)$$

The final form of the projection integral again is obtained by differentiation:

$$\begin{aligned} P_{\text{ac}\alpha}^{lm}(l_a, m_a; r_c) &= \frac{N(l_a, \alpha)}{(2\alpha)^{l_a}} \mathcal{Y}_{m_a}^{l_a}(\nabla_a) \left[\frac{P_{\text{ac}\alpha}^{lm}(0, 0; r_c)}{N(0, \alpha)} \right] \\ &= N(l_a, \alpha) \sqrt{4\pi(2l+1)} \exp[-\alpha(\mathbf{a} - \mathbf{c})^2] \\ &\times \sum_{l_1=0}^{l_a} \sum_{m_1} \varepsilon_{l_a l_1 m_a m_1} \mathcal{Y}_{m_a - m_1}^{l_a - l_1}(\mathbf{k}_a) \\ &\times r_c^{l_a - l_1} i_{l_1 + l_a - l_1}(k_a r_c) / k_a^{l_1 + l_a - l_1} I_{\text{ac}\alpha}^{lm}(l_1, m_1) \end{aligned} \quad (41)$$

with

$$\begin{aligned} I_{\text{ac}\alpha}^{lm}(l_1, m_1) &= \sum_{\lambda} \sum_{\mu} (-1)^{\mu} (2\lambda - 1)!! \varepsilon_{l_1 \lambda m_1 \mu} \varepsilon_{l \lambda m, -\mu} \\ &\times \mathcal{Y}_{m_1 - \mu}^{l_1 - \lambda}(\mathbf{c} - \mathbf{a}) \mathcal{Y}_{m + \mu}^{l - \lambda}(\mathbf{k}_a). \end{aligned} \quad (42)$$

Inserting Eq. (42) into the defining relation [Eq. (20)] yields the desired expression for W -type matrix elements with basis functions of arbitrary angular dependence:

$$\begin{aligned} W_{\text{abca}\beta\gamma}^{lm}(l_a, m_a; l_b, m_b) &= N(l_a, \alpha)N(l_b, \beta)D \\ &\times \sum_{l_1=0}^{l_a} \sum_{m_1} \varepsilon_{l_a l_1 m_a m_1} \mathcal{Y}_{m_a - m_1}^{l_a - l_1}(\mathbf{k}_a) \\ &\times \sum_{l_2=0}^{l_b} \sum_{m_2} \varepsilon_{l_b l_2 m_b m_2} \mathcal{Y}_{m_b - m_2}^{l_b - l_2}(\mathbf{k}_b) \end{aligned}$$

$$\begin{aligned} & \times 4\pi(2l+1)Q_{l+l_a-l_1, l+l_b-l_2}^{n+l_a+l_b-l_1-l_2}(k_a, k_b, \gamma)/k_a^{l+l_a-l_1}k_b^{l+l_b-l_2} \\ & \times \sum_m I_{\text{ac}\alpha}^{lm}(l_1, m_1)I_{\text{bc}\beta}^{lm}(l_2, m_2). \end{aligned} \quad (44)$$

This expression is very similar in structure to that obtained for V -type matrix elements with basis functions of arbitrary angular dependence [Eq. (34)]. It can be factorized in a very similar fashion, leaving at most simultaneous summation of seven significant angular momentum indices. The only major structural difference compared to Eq. (34) are the terms entering the innermost sum over m .

REAL SOLID HARMONICS

Thus far all equations have been presented for complex solid harmonics \mathcal{Y}_m^l . Defining the real solid harmonics $\bar{\mathcal{Y}}_\nu^l$, $\nu = 1, \dots, 2l+1$ by

$$\bar{\mathcal{Y}}_1^l = \mathcal{Y}_0^l, \quad (45)$$

$$\bar{\mathcal{Y}}_{2m}^l = (-1)^m \sqrt{2} \operatorname{Re} \mathcal{Y}_m^l, \quad m = 1, \dots, l, \quad (46)$$

$$\bar{\mathcal{Y}}_{2m+1}^l = (-1)^m \sqrt{2} \operatorname{Im} \mathcal{Y}_m^l, \quad m = 1, \dots, l, \quad (47)$$

one can transform all equations into a form suitable for these real solid harmonics by replacing the two key relations of the tensor coupling technique, the product rule [Eq. (6)] and differentiation rule [Eq. (7)], by their slightly more general counterparts:

$$\begin{aligned} \bar{\mathcal{Y}}_\nu^l(\nabla)[f(\mathbf{r})g(\mathbf{r})] &= \sum_{l'=0}^l \sum_{\nu', \nu''} \bar{\epsilon}_{ll'\nu\nu'} \bar{\mathcal{Y}}_{\nu'}^{l'}(\nabla)f(\mathbf{r}) \\ & \times [\bar{\mathcal{Y}}_{\nu''}^{l-l'}(\nabla)g(\mathbf{r})] \end{aligned} \quad (48)$$

and

$$\bar{\mathcal{Y}}_{\nu'}^{l'}(\nabla)\bar{\mathcal{Y}}_\nu^l(\mathbf{r}) = (2l-1)!! \bar{\epsilon}_{ll'\nu\nu'} \bar{\mathcal{Y}}_{\nu''}^{l-l'}(\mathbf{r}). \quad (49)$$

A new index ν'' has been introduced here to discriminate between the action on real and imaginary parts of \mathcal{Y}_m^l . However, not much computational effort results from the additional summation index ν'' since it takes only two values for nonvanishing coupling coefficients $\bar{\epsilon}_{ll'\nu\nu'}$.

Derivatives of the Matrix Elements

Determination of geometrical structures of molecules and clusters requires minimizing the total energy as a function of the atomic coordinates. Most automatic algorithms for geometry optimization are based on so-called quasi-Newton methods that utilize first-order derivatives (the gradients) of the

total energy with respect to nuclear displacements, i.e., the forces on the nuclei. Evaluating analytical forces within Kohn–Sham or Hartree–Fock theory is well established and has been implemented in many quantum chemistry codes [42–45]. Thus, we will refrain from repeating the formalism here, but merely mention that the presence of pseudopotentials requires all nuclear displacement derivatives of the two new types of matrix elements $V_{\text{ab}\alpha\beta,\gamma}^n$ and $W_{\text{ab}\alpha\beta,\gamma}^{ln}$ introduced above [Eqs. (18) and (20)]. Subsequently, the derivatives of these primitive matrix elements have to be treated in complete analogy to the derivatives of the nuclear potential.

First we would like to point out that evaluating nuclear displacement derivatives ∇_a , ∇_b , and ∇_c is equivalent to evaluating first-order real solid harmonics of the derivatives, $\bar{\mathcal{Y}}_m^1(\nabla_a)$, $\bar{\mathcal{Y}}_m^1(\nabla_b)$, and $\bar{\mathcal{Y}}_m^1(\nabla_c)$, since

$$\frac{\partial}{\partial x} = \bar{\mathcal{Y}}_2^1(\nabla), \quad \frac{\partial}{\partial y} = \bar{\mathcal{Y}}_3^1(\nabla), \quad \frac{\partial}{\partial z} = \bar{\mathcal{Y}}_1^1(\nabla). \quad (50)$$

Moreover, since the real solid harmonics $\bar{\mathcal{Y}}_m^1$ can easily be expressed by complex solid harmonics \mathcal{Y}_m^1 , it suffices to discuss the tensor derivatives $\mathcal{Y}_m^1(\nabla_a)$, $\mathcal{Y}_m^1(\nabla_b)$, and $\mathcal{Y}_m^1(\nabla_c)$. Inspection of Eqs. (34) and (44) reveals that besides solid harmonics of various simple arguments such as $\mathbf{c} - \mathbf{a}$ and $\mathbf{k}_b = 2\beta(\mathbf{b} - \mathbf{c})$, the only contributions to the V -type and W -type matrix elements are derivatives of the exponential prefactor D [Eq. (24)], and of the following two special combinations of Q integrals and powers of k values:

$$Q_l^{n+l}(k, \eta)/k^l \quad \text{and} \quad Q_{l_1 l_2}^{n+l_1+l_2}(k_1, k_2, \eta)/k_1^{l_1} k_2^{l_2}. \quad (51)$$

The nuclear displacement derivatives of the exponential prefactor follow directly from the theorem of Hobson [Eq. (4)]:

$$\mathcal{Y}_m^1(\nabla_a)D = -2\alpha \mathcal{Y}_m^1(\mathbf{a} - \mathbf{c})D, \quad (52)$$

$$\mathcal{Y}_m^1(\nabla_b)D = -2\beta \mathcal{Y}_m^1(\mathbf{b} - \mathbf{c})D, \quad (53)$$

$$\mathcal{Y}_m^1(\nabla_c)D = [-2\alpha \mathcal{Y}_m^1(\mathbf{c} - \mathbf{a}) - 2\beta \mathcal{Y}_m^1(\mathbf{c} - \mathbf{b})]D. \quad (54)$$

Of course, the sum over all three equations is zero because of the homogeneity of space. The derivatives of the one-index Q integrals $Q_l^{n+l}(k, \eta)/k^l$ have already been addressed (indirectly) during the derivation of the V -type integrals. Using the definition of the k -vector [Eq. (25)], $k = 2\alpha(\mathbf{a} - \mathbf{c}) + 2\beta(\mathbf{b} - \mathbf{c})$, the desired derivatives can directly be reduced to the differentiation relation given by Eq. (32):

$$\begin{aligned} \mathcal{Y}_m^1(\nabla_a)[Q_l^{n+l}(k, \eta)/k^l] \\ = 2\alpha \mathcal{Y}_m^1(\nabla_k)[Q_l^{n+l}(k, \eta)/k^l], \end{aligned} \quad (55)$$

$$\begin{aligned} \mathcal{Y}_m^1(\nabla_b)[Q_i^{n+l}(k, \eta)/k^l] \\ = 2\beta \mathcal{Y}_m^1(\nabla_k)[Q_i^{n+l}(k, \eta)/k^l], \end{aligned} \quad (56)$$

$$\begin{aligned} \mathcal{Y}_m^1(\nabla_c)[Q_i^{n+l}(k, \eta)/k^l] \\ = -2(\alpha + \beta) \mathcal{Y}_m^1(\nabla_k)[Q_i^{n+l}(k, \eta)/k^l]. \end{aligned} \quad (57)$$

Again, the three equations add up to zero. For two-index Q integrals, a relation analogous to that for the one-index Q integrals [Eq. (32)], exists; for example:

$$\begin{aligned} \mathcal{Y}_m^l(\nabla_{k_1})[Q_{l_1 l_2}^{n+l_1+l_2}(k_1, k_2, \eta)/k_1^{l_1} k_2^{l_2}] \\ = \mathcal{Y}_m^l(\mathbf{k}_1) Q_{l_1 l_2}^{n+l_1+l_2}(k_1, k_2, \eta)/k_1^{l_1+l_1} k_2^{l_2}. \end{aligned} \quad (58)$$

Hence, expressions for the nuclear displacement derivatives of two-index Q integral contributions to W -type matrix elements follow in similar fashion. Finally, the derivatives of the solid harmonics are obtained directly from the differentiation rule of the tensor coupling technique [Eq. (7)]. Thus, having established the nuclear displacement derivatives of all contributions to V -type and W -type matrix elements, it is straightforward (by direct differentiation) to derive the corresponding formulas for the analytical forces from the closed analytical expressions of these matrix elements. We refrain from presenting these lengthy expressions.

Results

Next, we will report results for the pseudopotential (PP) implementation in our parallel density

functional code PARAGAUSS [22, 23] as obtained on sample systems. We will focus on the obtained speed-up compared to all-electron (AE) calculations. Accuracy aspects are briefly touched as well. Since PARAGAUSS provides a scalar-relativistic all-electron treatment, we also compare results of such calculations on compounds with heavy elements to those of nonrelativistic calculations employing relativistic pseudopotentials. The set of test molecules was chosen to build a representative sample of systems recently treated in our research group [46–53].

For all calculations the exchange-correlation functional, as suggested by Becke and Perdew [54–56], was applied self-consistently. Automatic geometry optimizations were carried out by means of analytical first-order energy derivatives. The sizes of the employed all-electron orbital basis sets and their origin are summarized in the left panel of Table I. These basis sets were subject to generalized contractions based on atomic Kohn–Sham eigenvectors. The resulting all-electron orbital basis sets are those routinely used in our research group.

For the pseudopotential calculations the scheme commonly known as LanL2DZ [57] was widely adopted (except for uranium). These pseudopotentials were originally generated for Hartree–Fock calculations. However, it has been shown (e.g., [27, 28]) that such pseudopotentials also perform well in combination with density functional methods. In the LanL2DZ scheme, electrons of H and first-row elements are treated explicitly using all-electron ba-

TABLE I _____
Sizes of the uncontracted (in parenthesis) and contracted (in brackets) Gaussian orbital basis sets used for the all-electron (AE) and the pseudopotential (PP) calculations.^a

Element	AE		PP		
	Basis	Ref.	Basis	Z_{core}	Ref.
H	(6, 1) → [3, 1]	[68, 69]	(4, 1) → [3, 1]		[58]
C,N,O	(9, 5, 1) → [5, 4, 1]	[68, 69]	(9, 5, 1) → [4, 2, 1]		[58]
F	(9, 5, 1) → [5, 4, 1]	[70]	(3, 3, 1) → [2, 2, 1]	10	[58]
Mg	(15, 10, 1) → [6, 5, 1]	[71]	(3, 3) → [2, 2]	10	[36]
Al,Si	(12, 9, 1) → [6, 4, 1]	[72, 73]	(3, 3, 1) → [2, 2, 1]	10	[36, 58]
S,P	(12, 9, 2) → [6, 5, 2]	[69, 72]	(3, 3, 1) → [2, 2, 1]	10	[36, 58]
Ni	(15, 11, 6) → [7, 6, 3]	[74, 75]	(5, 5, 5) → [3, 3, 2]	10	[37]
Mo	(19, 14, 9) → [8, 6, 5]	[69, 76]	(5, 6, 4) → [3, 3, 2]	28	[36]
Re	(21, 17, 12, 7) → [9, 8, 5, 2]	[68]	(5, 6, 3) → [3, 3, 2]	60	[37]
Os	(21, 17, 12, 7) → [9, 8, 5, 2]	[49, 77]	(5, 6, 3) → [3, 3, 2]	60	[37]
Au	(19, 15, 10, 6) → [11, 10, 7, 3]	[78, 79]	(5, 6, 3) → [3, 3, 2]	60	[37]
U	(24, 19, 16, 11) → [10, 7, 7, 4]	[61]	(6, 5, 2, 4) → [3, 3, 2, 2]	60	[60]

^a The number Z_{core} of core electrons and the origin of the basis sets are also given.

sis sets of Dunning and Hay [58]. For other atoms (except U) the pseudopotentials and the orbital basis sets due to Hay and Wadt were employed [36, 37]. In case of transition metal elements, so-called small core potentials were chosen. These basis sets were augmented by polarization exponents, one p exponent in case of H, and one d exponent in case of first- and second-row main group elements (except for Mg) [58] (PP + D95*). All these orbital basis sets were subject to segmented contractions as indicated in the right panel of Table I (for details see Ref. [59]). For U, the PP and orbital basis set due to Hay and Martin were used (PP + HM) [60].

In several quantum chemical programs, especially in those designed for density functional (DF) calculations, an auxiliary basis set of atom-centered real spherical Gaussians is used to represent the charge density. In this way the calculation of four-center integrals which occur in traditional schemes, can be avoided [23, 62–66]. This technique is also used in the program PARAGAUSS. One strategy for constructing such auxiliary (or fitting) basis sets is to scale exponents of the orbital basis set by a factor of 2 [62–64], i.e., to generate one such spherical fitting function for every s - and p -type orbital Gaussian exponent; the fitting basis functions derived from p -type exponents were taken to exhibit an additional radial prefactor r^2 [62–64]. To achieve angular flexibility, polarization functions [with higher angular momentum were added to these auxiliary basis sets [with exponents 0.1, 0.25, 0.625, 1.5625, 3.90625 for p - and 0.2, 0.50, 1.25, 3.125, 7.8125 for d - polarization (not used for H)] [62–64]. This specific recipe was applied to all all-electron basis sets adopted in this study. However, for smaller basis sets such as those commonly used in pseudopotential calculations, this procedure did not yield adequate auxiliary basis sets. Therefore, a different strategy was adopted for generating auxil-

iary basis sets, namely Gaussian exponents of s -type fitting functions were obtained by minimizing the Coulomb self-interaction energy of the difference between the fitted charge density and a spherically symmetric reference charge density. That energy expression yields the characteristic correction term of the total energy when establishing the fitting-function strategy [64]. An atomic calculation with a huge, converged auxiliary basis set serves as reference in the minimization process, thus avoiding four-center integrals. It turned out that use of r^2 -type auxiliary functions did not result in smaller fitting basis sets; rather, in some cases, such functions tend to impede self-consistent field (SCF) convergence. Therefore, we refrained from employing r^2 -type fitting functions in this second recipe. As polarization functions, the same set of $5p$ and $5d$ functions (see above) were used as in the all-electron basis sets.

We checked the accuracy of our pseudopotential implementation by comparing results on the sample system H_3PAuSH [46] to those obtained with the program Gaussian94 [67], which does not employ auxiliary basis sets. Both program packages yielded very similar results (see Table II), confirming the overall correctness of our pseudopotential implementation and the quality of the auxiliary basis sets used. However, the agreement of pseudopotential calculations with scalar-relativistic PARAGAUSS all-electron calculations (also listed in Table II) is rather poor. To check whether these findings are related to the Au pseudopotential itself or to the smaller orbital basis set normally used with these pseudopotentials, an additional pseudopotential test calculation was performed where the original PP basis sets were replaced by the large all-electron orbital and fitting basis sets (PARAGAUSS PP + AE basis). Only small deviations from the all-electron results are found in that test calculation (see Table II). This

TABLE II
Comparison of structure parameters and binding energies of H_3PAuSH [38] as calculated with the programs PARAGAUSS and Gaussian94.^a

	$d(\text{Au-S})$	$d(\text{Au-P})$	$d(\text{S-H})$	$d(\text{P-H})$	$\angle(\text{Au-S-H})$	BE
PARAGAUSS AE	2.304	2.266	1.360	1.425	95.1	3.78
PARAGAUSS PP + D95*	2.337	2.314	1.376	1.431	94.0	3.45
Gaussian94 PP + D95*	2.340	2.313	1.376	1.431	94.0	3.38
PARAGAUSS PP + AE basis	2.311	2.270	1.367	1.430	94.9	3.72

^a Bond lengths in angstroms, angles in degree. The binding energies (BE, in electron volts) are given relative to the energy of the fragments H_3PAu and SH.

TABLE III
Comparison of selected bond lengths (d , in angstroms) and binding energies (BE, in electron volts) per “ligand” of various compounds.

	SiH ₄		Ni(CO) ₄			UF ₆	
	$d(\text{Si-H})$	BE	$d(\text{Ni-C})$	$d(\text{C-O})$	BE	$d(\text{U-F})$	BE
PARAGAUSS AE	1.495	3.51	1.778	1.154	1.98	2.030	6.16
PARAGAUSS PP + D95*/HM	1.495	3.51	1.785	1.163	1.98	2.040	5.49

finding suggests that the quality of the orbital basis set normally provided for pseudopotentials limits the overall accuracy much more strongly than the pseudopotential itself.

Inspection of the other examples, small molecules: SiH₄, Ni(CO)₄, and UF₆ (Table III), adsorption systems: Re(CO)₃/Mg₆O₃ (Table IV) [47], and C₆H₆/Si₁₃H₁₂ (Table V) [48], a ligated metal cluster: Os₃(CO)₁₂ (Table VI) [49], and a metal carbene complex: Pd(C₃N₂H₄)₂ (Table VII), which was studied in the context of Heck reactions [50], reveals that on average the agreement between pseudopotential and the corresponding all-electron calculations is a few hundredth of an angstrom for bond lengths, and several tenth of an electron volt for binding energies. These findings are in line with similar comparative studies on transition metal complexes [28] where differences in the order of some pm for bond lengths and a few millihartrees in binding energies are reported. As a general trend we observe that the C–O bond length in carbonyl ligands is always shortened by the use of pseudopotentials on the coordinated metal atoms, whereas the M–C distances are elongated. The largest deviations in geometry and binding energy (BE) were found for H₃PAuSH [$\Delta d(\text{Au-P}) = 0.05 \text{ \AA}$] and UF₆ ($\Delta \text{BE} = 0.67 \text{ eV}$), respectively. These discrepancies might be taken as indicators of some systematic problems either with the basis sets, the pseudopotentials, or the nonrelativistic treatment of valence electrons for strongly relativistic elements.

Next, we discuss the computational savings connected with the usage of pseudopotentials. When discussing speed-ups of pseudopotential calculations, one has to keep in mind that savings are mostly related to the smaller number n_{elec} of electrons treated explicitly and the reduced sizes of the orbital (n_{orb}) and auxiliary (n_{fit}) basis sets. As a consequence larger speed-ups are expected for heavy-element compounds with large numbers of core electrons. The results of our benchmark calculations together with the characteristic dimensions of the compounds investigated are given in Table VIII. Beside the sample systems already mentioned, it contains benchmarks for a zeolite model cluster: AlSi₅O₆H₁₂ [51], a gold thiolate cluster: Au₁₃(SH)₈ [52], and a model for an active site of a Mo-S enzyme: [(HOCHO)(SH)OMoS₂C₂H₂][−] [53]. The implementation of the pseudopotentials are fully compatible with the special design of PARAGAUSS to efficiently use a large number of processors in parallel. However, to facilitate the analysis of the CPU timings, all calculations reported here were carried out on a single R10000 CPU of a SGI Power Challenge.

The speed-up of the SCF part is easily estimated. Assuming that the most time-consuming steps are the setup of the electron density on the integration grid and the numerical evaluation of the matrix elements of the exchange-correlation potential, speed-up values should be close to the ratio of $n_{\text{orb}}n_{\text{elec}}$ or n_{orb}^2 , respectively, for the AE and PP calculations.

TABLE IV
Comparison of structure parameters and adsorption energies (BE) of Re(CO)₃/Mg₆O₃ [39].^a

	$d(\text{Re-O})$	$d(\text{Re-C})$	$d(\text{C-O})$	$d(\text{O-Mg1})$	$d(\text{O-Mg2})$	$\angle(\text{Re-C-O})$	BE(eV)
PARAGAUSS AE	2.151	1.953	1.165	2.041	2.082	179.2	8.09
PARAGAUSS PP + D95*	2.150	1.945	1.175	2.030	2.081	179.7	8.35

^a The cluster Mg₆O₃ models a cationic corner defect site; it is embedded in an array of $10 \times 10 \times 10$ point charges (PC, $q = \pm 2e$) to reproduce the surface Madelung field [39]. Bond lengths in angstrom, angles in degree, binding energies in electron volts.

TABLE V
Comparison of structure parameters and adsorption energies (BE) of C₆H₆/Si₁₃H₁₂.^a

	$d(\text{C-C})$	$d(\text{C}_d\text{-C})$	$d(\text{C}_d\text{-Si}_d)$	$d(\text{Si}_d\text{-Si}_d)$	$d(\text{Si}_d\text{-Si})$	BE
PARAGAUSS AE	1.350	1.510	1.967	2.448	2.370	1.42
PARAGAUSS PP + D95*	1.358	1.516	1.961	2.442	2.364	1.62

^a This cluster model was employed in a study of benzene adsorption on the Si(001) surface [40]. Bond lengths in angstroms, binding energies in electron volts.

Actually the speed-up values are somewhat smaller (see Table VIII), reflecting that other parts with a more favorable scaling with system size (such as the evaluation of the individual basis functions on the numerical grid) also contribute to the timing.

The speed-up values of the integral part are more difficult to rationalize. In general, the smaller the orbital and auxiliary basis set, the fewer matrix elements have to be evaluated. Thus for compounds with heavy elements such as H₃PAuSH [46] and Re(CO)₃/Mg₆O₃ + PC [47], speed-up values close to 10 were observed. However, one also has to keep in mind the extra cost of evaluating the pseudopotential matrix elements. This is very clearly demonstrated for the example of the gold-thiolate cluster Au₁₃(SH)₈ [52]. Although the number of orbital basis functions is reduced by a factor of 3.6 when switching to a pseudopotential calculation, the overall speed-up of the integral part reaches just 2.3. This is due to the fact that the cluster is dominated by Au atoms; for Au atoms (in contrast to the lighter elements) a pseudopotential with projectors up the $L = 3$ entails a significant computational effort. All-electron test calculations with the pseudopotential basis sets actually resulted in speed-up values above 20, confirming the notable computational effort for evaluating the pseudopotential matrix elements of that special system.

Calculation of forces requires both analytical evaluation of matrix elements as in the integral part

and numerical integration which dominates the SCF part. Hence arguments similar to those already discussed can be applied to rationalize the timings observed for the evaluation of the forces.

Finally, we note that for those systems, which require a scalar-relativistic all-electron treatment (marked by rel. in Table VIII), the speed-up values also contain the savings due to the nonrelativistic treatment of the valence electrons, which is justified when using pseudopotentials.

Summary

The tensor coupling technique developed for an efficient evaluation of matrix elements with Gaussian-type *solid harmonics* of arbitrary angular momentum has successfully been applied to evaluate matrix elements of analytical pseudopotentials. By taking advantage of standard recursion relations for modified spherical Bessel functions, closed analytical expressions have been derived that are based on integrals over products of modified spherical Bessel functions and algebraic and/or exponential functions. These integrals are already known from the evaluation of pseudopotential matrix elements with *Cartesian* Gaussians.

For the evaluation of analytical forces, it is necessary to compute the nuclear displacement derivatives of the pseudopotential matrix elements. We showed that these derivatives can be obtained in a

TABLE VI
Comparison of bond lengths (d , in angstroms) and average binding energies (BE, in electron volts) per CO ligand of the cluster compound Os₃(CO)₁₂ (D_{3h} symmetry) [41].^a

	$d(\text{Os-Os})$	$d(\text{Os-C})$	$d(\text{C-O})$	BE
PARAGAUSS AE	2.957	1.961/1.912	1.160/1.164	2.16
PARAGAUSS PP + D95*	2.964	1.960/1.926	1.166/1.170	2.28

^a The first $d(\text{Os-C})$ and $d(\text{C-O})$ values refer to the out-of-plane ligands, the second to the in-plane ligands.

TABLE VII
Comparison of bond distances (in angstroms) of the carbene complex Pd(C₃N₂H₄)₂ (D_{2h}) [42].^a

	<i>d</i> (Pd-C)	<i>d</i> (C-N)	<i>d</i> (C-H)
PARAGAUSS AE	2.016	1.409	1.086/1.087
PARAGAUSS PP + D95*	1.971	1.412	1.090/1.090

^a The distance *d*(C-H) refer to nonequivalent hydrogen centers.

straightforward manner by employing differential relations already introduced for the evaluation of the pseudopotential matrix elements themselves.

A set of sample molecules and cluster models, which are typically used in our research group, has been used to test the implementation in the parallel density functional program PARAGAUSS [22, 23]. The efficiency of the implementation as well as the capability to reproduce all-electron results have

TABLE VIII
Comparison of timings and characteristic system dimensions between all-electron (AE) calculations and pseudopotential (PP) calculations.^a

		Timing			Dimensions		
		Integral	SCF	Forces	<i>n</i> _{fit}	<i>n</i> _{orb}	<i>n</i> _{elec}
UF ₆ (rel.)	AE	45	1.3	165	57	226	146
	PP	5.7	0.77	18	26	126	68
	Ratio	7.9	1.67	9.2	2.2	1.8	2.1
Pd(C ₃ N ₂ H ₄) ₂	AE	54	40	375	167	321	118
	PP	27	23	269	121	212	90
	Ratio	2.0	1.7	1.4	1.4	1.5	1.3
Ni(CO) ₄	AE	10	13	106	74	216	84
	PP	5.3	8.3	76	41	142	74
	Ratio	1.9	1.6	1.4	1.8	1.5	1.1
H ₃ PAuSH (rel.)	AE	88	38	235	195	187	114
	PP	10	8.9	60	129	68	34
	Ratio	8.8	4.3	3.9	1.5	2.7	3.3
C ₆ H ₆ /Si ₁₃ H ₁₂	AE	431	300	2704	435	580	236
	PP	300	138	1850	331	349	106
	Ratio	1.4	2.2	1.5	1.3	1.7	2.2
Re(CO) ₃ /Mg ₆ O ₃ (rel.) + PC	AE	2178	152	10450	203	438	205
	PP	219	42	839	172	205	85
	Ratio	9.9	3.6	12.4	1.2	2.1	2.4
Os ₃ (CO) ₁₂ (rel.)	AE	360	163	2604	199	744	396
	PP	167	78	1010	149	426	215
	Ratio	2.2	2.1	2.6	1.3	1.7	1.8
AlSi ₅ O ₆ H ₁₂	AE	875	466	1867	924	342	142
	PP	357	227	1403	751	228	84
	Ratio	2.4	2.0	1.3	1.2	1.5	1.7
Au ₁₃ (SH) ₈ (rel.)	AE	1005	442	7960	186	1565	1163
	PP	430	60	1530	103	430	303
	Ratio	2.3	7.4	5.2	1.8	3.6	3.8
[(HOCHO)(SH)OMoS ₂ C ₂ H ₂] ⁻	AE	582	179	814	683	311	138
	PP	179	63	490	541	176	80
	Ratio	3.2	2.8	1.7	1.3	1.8	1.7

^a All timings (in CPU seconds) have been obtained using a single SGI R10000 CPU; for the SCF part, CPU times per SCF cycle are given. *n*_{fit} denotes the number of charge fitting functions, *n*_{orb} the total number of contracted orbital basis functions, and *n*_{elec} the number of the electrons treated explicitly.

been considered. Depending on the size of the basis sets and the number of core electrons, speed-up values up to a factor of about 10 were achieved. Deviations in the binding energies are found to be in the order of several tenths of an electron volt; bond lengths are reproduced with an accuracy of a few hundredths of an angstrom. Deviations, especially in the binding energy, are found to be somewhat larger for compounds that contain strongly relativistic elements.

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