

# **Ab initio energy-adjusted pseudopotentials for the noble gases Ne through Xe: Calculation of atomic dipole and quadrupole polarizabilities**

Andreas Nicklass, Michael Dolg,<sup>a)</sup> Hermann Stoll, and Heinzwerner Preuss  
*Institut für Theoretische Chemie der Universität Stuttgart, 70550 Stuttgart, Germany*

(Received 1 February 1995; accepted 27 February 1995)

Nonrelativistic and one-component relativistic energy-adjusted *ab initio* pseudopotentials for the noble gases neon through xenon are presented together with corresponding optimized valence basis sets. To account for nonscalar relativistic effects the relativistic pseudopotentials are supplemented with effective spin-orbit potentials. The reliability of the presented pseudopotentials is demonstrated in atomic test calculations on ionization potentials and spin-orbit splittings in comparison with nonrelativistic and relativistic all-electron calculations as well as experimental data. Together with extended valence basis sets the pseudopotentials are applied in calculations on the static dipole and quadrupole polarizabilities of the noble gas atoms. The best values, computed at the coupled-cluster level of theory [CCSD(T)], for the dipole and quadrupole polarizabilities of the noble gases are  $2.69a_0^3$  and  $7.52a_0^5$  for Ne,  $11.07a_0^3$  and  $52.25a_0^5$  for Ar,  $17.06a_0^3$  and  $97.39a_0^5$  for Kr, and  $27.66a_0^3$  and  $209.85a_0^5$  for Xe. © 1995 American Institute of Physics.

## **I. INTRODUCTION**

Nowadays the use of pseudopotentials (PP) or effective core potentials (ECP) to exclude the inactive atomic core electrons from an explicit treatment in quantum chemical calculations is well established. The development and application of such potentials has been outlined in several review articles.<sup>1-3</sup> Besides the saving of computer time and the reduction of memory requirements in comparison to all-electron calculations, the pseudopotential method constitutes a reliable and convenient technique to incorporate the major scalar relativistic effects into calculations with commonly used quantum chemistry programs such as COLUMBUS,<sup>4</sup> GAMESS,<sup>5</sup> GAUSSIAN,<sup>6</sup> MOLPRO,<sup>7</sup> or TURBOMOLE.<sup>8</sup>

During the past decade several compilations of effective core potentials, pseudopotentials, and model potentials have been published. Whereas the model potentials of Huzinaga and collaborators<sup>9-11</sup> retain the nodal structure of the valence orbitals in the core region, pseudopotentials or effective core potentials rely on the pseudo-orbital transformation. This means that the radial nodes of the valence orbitals in the core region are removed and thus there is no need for basis functions to model these nodes as in all-electron or model potential calculations. Therefore, the computational effort for the integral evaluation and transformation steps decreases drastically in many cases. Different schemes for the generation of pseudopotentials have been proposed by several groups.

In the shape-consistent procedure<sup>12,13</sup> the potentials are generated on a numerical grid by inverting (one-electron) Fock equations for pseudo-orbitals derived from numerical atomic wave functions. The numerically tabulated potentials are fitted with analytic Gaussian expansions. Because of the complex shape, accurate fits of the radial potentials often require as many as eight Gaussian functions. Widely used sets of *ab initio* shape-consistent effective core potentials

have been published by Hay and Wadt,<sup>14-16</sup> and Christiansen and co-workers.<sup>17-21</sup>

More compact analytic potentials have been generated by Stevens *et al.*<sup>22-24</sup> by means of an alternative fit procedure, which relies on a functional based on orbital overlap and eigenvalue differences.<sup>25</sup> Like the shape-consistent potentials these compact effective core potentials are based on nonobservable quantities as orbital densities and energies taken from a single reference state of the atom.

In contrast to this, the procedure developed by our group<sup>26,27</sup> relies on the fit of the pseudopotential parameters to the valence energies of several neutral and ionic atomic states in a least-squares sense, leading to energy-adjusted pseudopotentials. In this paper we present nonrelativistic and relativistic *ab initio* pseudopotentials representing the  $\text{Ng}^{8+}$  cores of the noble gases Ne through Xe. Similar pseudopotentials have previously been generated in our group for other elements of the Periodic Table: Pseudopotentials for the main-group elements Hg through Rn were published by Küchle *et al.*;<sup>28</sup> Bergner *et al.*<sup>29</sup> presented parameter sets of relativistic pseudopotentials for the other elements of Groups 13 through 17. Prior to these publications we presented pseudopotentials for the first row transition elements,<sup>27</sup> the lanthanides,<sup>30,31</sup> and the second and third row transition elements.<sup>32</sup> Recently we could derive pseudopotentials for the actinides<sup>33</sup> and for hahnium ( $Z=105$ ).<sup>34</sup> By means of systematic calibration studies<sup>35-37</sup> we demonstrated the reliability of our energy-adjusted *ab initio* pseudopotentials in comparison with all-electron calculations. (A compilation of our pseudopotential parameters and optimized valence basis sets in plain ASCII format, including the semi-empirical pseudopotentials of Fuentealba *et al.*<sup>38-40</sup> and Igel-Mann *et al.*,<sup>41</sup> can be obtained on request from h.stoll@rus.uni-stuttgart.de.)

For efficient use of the presented pseudopotentials in molecular calculations optimized atomic valence basis sets have to be supplied. When preparing basis sets, we had to consider several points. First of all the errors in excitation energies at the self-consistent field (SCF) level that occur

<sup>a)</sup>Present address: Max-Planck-Institut für Physik komplexer Systeme (Dresden), Aussenstelle Stuttgart, Heisenbergstr. 1, 70569 Stuttgart, Germany.

through the introduction of a finite basis set should not exceed the pseudopotential errors. For efficiency the number of Gaussian primitives has to be kept small and a contraction scheme has to be introduced in such a way that the ability to accurately predict the term energies of low-lying neutral and ionic states of the atom is not lost. The bonding of noble gas atoms in molecules or clusters is mainly due to dispersion effects. Therefore, a convenient basis set has to be capable of reproducing the atomic polarizabilities.

Section II of this paper is divided into four subsections which are devoted to our fitting procedure for the energy-adjusted pseudopotentials, the generation of the corresponding spin-orbit operators, the presentation of the optimized valence basis sets, and finally the adjustment of effective core polarization potentials which supplement the relativistic  $\text{Xe}^{8+}$  pseudopotential in order to account for core-valence correlation effects.<sup>42</sup>

To test the reliability of the presented energy-adjusted *ab initio* pseudopotentials and the optimized valence basis sets we performed calculations on atomic ionization potentials and excitation energies. In Sec. III we report on the comparison of the results of these calculations with corresponding all-electron calculations as well as experimental data. In Sec. IV we apply the presented pseudopotentials in an investigation on the static dipole and quadrupole polarizabilities of the noble gas atoms. Finally, Sec. V contains our conclusions.

Prior to their publication these pseudopotentials were employed in investigations on the molecular structures of noble gas hexafluorides  $\text{NgF}_6$ ,<sup>43</sup> on interaction energies between noble gas atoms and floppy molecules,<sup>44</sup> on Ba-noble gas diatomic complexes,<sup>45</sup> and on BeO-noble gas complexes.<sup>46</sup>

## II. PSEUDOPOTENTIALS AND BASIS SETS

### A. Pseudopotentials

Elimination of the core electrons from the explicit treatment in quantum chemical calculations leads to a molecular valence Hamiltonian (atomic units are used throughout this paper):

$$\hat{H} = -\frac{1}{2} \sum_i \Delta_i + \sum_{i < j} \frac{1}{r_{ij}} + \sum_{\lambda < \mu} \frac{Q_\lambda Q_\mu}{R_{\lambda\mu}} + \sum_{\lambda, i} V_{\text{PP}}^{(\lambda)}(\mathbf{r}_i) + \sum_{\lambda, i} V_{\text{SO}}^{(\lambda)}(i) + \sum_{\lambda} V_{\text{CPP}}^{(\lambda)},$$

where the indices  $i, j$  denote the valence electrons and  $\lambda, \mu$  are the indices of the atomic cores or nuclei.  $Q_\lambda$  and  $Q_\mu$  represent the corresponding core charges,  $V_{\text{SO}}^{(\lambda)}$  the two-component spin-orbit operators (cf. Sec. II B), and  $V_{\text{CPP}}^{(\lambda)}$  the effective core polarization potentials (cf. Sec. II D).  $V_{\text{PP}}^{(\lambda)}$  are spin-orbit averaged pseudopotentials of the semilocal form

$$V_{\text{PP}}^{(\lambda)}(\mathbf{r}_i) = -\frac{Q_\lambda}{r_{i\lambda}} + \sum_{l=0}^{l_{\text{max}}} \left[ \sum_k B_{lk}^{(\lambda)} \exp(-\beta_{lk}^{(\lambda)} r_\lambda^2) \right] \mathcal{A}_l^{(\lambda)}, \quad W = \sum_n [E_n^{\text{PP, val}} - E_n^{\text{AE, val}}]^2$$

where  $\mathcal{A}_l^{(\lambda)}$  stands for the projection operator onto the Hilbert subspace of angular symmetry  $l$  with respect to center  $\mathbf{R}_\lambda$ :

$$\mathcal{A}_l^{(\lambda)} = \sum_{m=-l}^l |Y_{lm}^{(\lambda)}\rangle \langle Y_{lm}^{(\lambda)}|.$$

In the case of the noble gas atoms the valence shell comprises eight electrons and hence  $Q_\lambda = 8$ . The parameter  $l_{\text{max}}$  has been chosen to be 2 for Ne, 3 for Ar, and 4 for Kr and Xe. Deviations of the semilocal pseudopotentials for  $l > l_{\text{max}}$  from the point charge approximation proved to be negligible with respect to the resulting valence energies. The index  $k$  is limited to be 1 or 2.

The  $B_{lk}^{(\lambda)}$  and  $\beta_{lk}^{(\lambda)}$  constitute the adjustable parameters of the ansatz for the spin-orbit averaged pseudopotentials. The reference data used to determine these parameters consist in total valence energies taken from numerical  $LS$ -coupled non-relativistic (Hartree-Fock, HF) or relativistic (Wood-Boring, WB) all-electron calculations on a variety of energetically low-lying electronic states of the neutral noble gas atoms and their singly charged ions. To illustrate our choice of reference energies we list as an example the 18 atomic states used to determine the Ne pseudopotentials:  $2s^2 2p^6 ({}^1S)$ ,  $2s^2 2p^5 3s^1 ({}^3P)$ ,  $2s^2 2p^5 3p^1 ({}^3D)$ ,  $2s^2 2p^5 3d^1 ({}^3F)$ ,  $2s^2 2p^5 4s^1 ({}^3P)$ ,  $2s^2 2p^4 3s^2 ({}^3P)$ ,  $2s^2 2p^4 3p^2 ({}^5D)$ ,  $2s^2 2p^4 3d^2 ({}^5G)$ ,  $2s^2 2p^4 4s^2 ({}^3P)$ ,  $2s^1 2p^6 3s^1 ({}^3S)$ ,  $2s^1 2p^6 3p^1 ({}^3P)$ ,  $2s^1 2p^6 3d^1 ({}^3D)$ ,  $2s^1 2p^6 4s^1 ({}^3S)$ ,  $2s^2 2p^5 ({}^2P)$ ,  $2s^2 2p^4 3s^1 ({}^4P)$ ,  $2s^2 2p^4 3p^1 ({}^4D)$ ,  $2s^2 2p^4 3d^1 ({}^4F)$ , and  $2s^1 2p^6 ({}^2S)$ . In the case of the heavier noble gas atoms Ar through Xe the parts of the pseudopotentials with  $l > 2$  are adjusted to reference valence energies which have been derived from atomic calculations on several (one valence electron) states of the corresponding  $\text{Ng}^{7+}$  ions.

The atomic all-electron calculations needed to derive the reference valence energies for the pseudopotential adjustments are carried out numerically. For that purpose we use a modified version of the finite-difference Hartree-Fock program MCHF77 of Froese Fischer.<sup>47</sup> In order to incorporate the major scalar relativistic effects into our reference data we use a scheme similar to that proposed by Cowan and Griffin<sup>48</sup>: The nonrelativistic Fock operator is supplemented with a mass-velocity term and a Darwin term as suggested by Wood and Boring.<sup>49</sup> These terms can be derived from the single-particle central-field Dirac equation by eliminating the small component and averaging over the spin-orbit splitting. Details of the implementation of this so-called Wood-Boring equation and its accuracy can be found elsewhere.<sup>28,30</sup>

With the all-electron reference values  $E^{\text{AE, val}}$  for the valence energies at hand, the pseudopotential parameters  $B_{lk}^{(\lambda)}$  and  $\beta_{lk}^{(\lambda)}$  are adjusted in such a manner that the valence energies  $E^{\text{PP, val}}$  obtained in numerical pseudopotential calculations agree in a least-squares sense with the corresponding reference energies. Thus the functional

TABLE I. Parameters (in atomic units) of the nonrelativistic and relativistic pseudopotentials and the corresponding spin-orbit operators for the noble gases Ne, Ar, Kr, and Xe.

Ng	$Q$	$l$	$k$	Nonrelativistic PP		Relativistic PP		
				$B_{lk}$	$\beta_{lk}$	$B_{lk}$	$\Delta B_{lk}$	$\beta_{lk}$
Ne	8	0	1	112.528 224 60	32.029 855	112.525 435 66		31.860 162
			2	28.445 896 04	12.294 136	28.300 834 54		12.362 219
		1	1	-10.939 828 72	21.525 406	-11.126 585 43	0.122 052 30	21.508 034
			2	3.394 260 49	13.091 176	3.387 549 19	0.024 134 63	12.910 447
			1	-0.164 096 78	0.850 385	-0.184 089 21	0.001 033 12	0.850 385
Ar	8	0	1	68.693 278 18	10.291 970	68.667 788 01		10.261 721
			2	24.488 142 03	3.947 937	24.042 766 29		3.952 725
		1	1	27.596 721 44	5.388 907	27.730 763 31	-0.058 917 37	5.392 714
			2	4.136 546 27	2.704 463	4.045 459 04	0.165 438 79	2.699 967
			1	-8.140 253 35	8.084 705	-8.137 476 96	-0.077 239 97	8.086 235
		2	2	-1.662 417 08	4.018 469	-1.664 528 08	0.044 589 90	4.016 632
			1	-3.409 226 53	5.295 301	-3.400 098 45	0.147 135 89	5.208 459
Kr	8	0	1	92.650 978 22	5.992 118	73.915 693 90		5.877 718
			2	12.406 821 35	2.740 117	16.168 250 80		3.084 622
		1	1	43.027 088 82	4.765 412	58.517 691 01	-1.864 461 70	5.164 110
			2	10.628 567 05	2.496 194	8.259 100 73	1.351 241 30	2.358 302
			1	18.649 044 58	2.807 086	33.458 227 76	0.179 544 45	3.215 362
		2	2	2.947 348 84	1.914 634	0.677 253 31	0.083 230 32	1.285 008
			1	-15.239 787 48	4.094 109	-15.158 698 59	0.069 658 42	4.082 869
		3	2	-0.193 582 05	1.243 945	-0.174 088 25		1.193 960
			1			-6.833 158 77		3.180 775
Xe	8	0	1	122.762 313 71	3.815 600	122.763 829 34		3.940 263
			2	8.201 354 56	1.878 604	8.308 851 15		2.277 264
		1	1	68.757 319 63	3.003 078	68.823 004 37	-1.746 091 13	3.028 373
			2	3.640 848 71	1.283 819	3.646 742 23	2.194 872 57	1.394 319
			1	23.083 198 30	2.027 610	23.652 078 54	-1.045 675 91	2.122 605
		2	2	3.172 988 23	0.830 435	3.258 441 13	0.271 992 91	0.798 669
			1	-48.302 017 24	6.246 157	-47.703 198 76	0.207 722 07	6.164 360
		3	2	-6.915 728 92	1.564 998	-6.541 139 91		1.542 374
			1			-7.105 850 60		1.847 892

(where the sum is over all reference states) has to be minimized with respect to the pseudopotential parameters; this is achieved by the quasi-Newton method of Murtagh and Sargent.<sup>50</sup> The mean deviation between an all-electron valence energy and the corresponding pseudopotential value is typically of the order of 10 meV. The error of the difference between any two of the reference state valence energies calculated with these energy-adjusted pseudopotentials is in all cases less than 50 meV. The derived parameters of the nonrelativistic and relativistic pseudopotentials are listed in Table I.

## B. Spin-orbit operators

A convenient form of the spin-orbit operator to be used in addition to the one-component relativistic pseudopotentials is the one proposed by Pitzer and Winter<sup>51</sup>:

$$V_{SO}^{(\lambda)}(i) = \sum_{l=1}^{l'_{\max}} \frac{2\Delta V_{SO,l}^{(\lambda)}(r_{i\lambda})}{2l+1} \mathcal{P}_l^{(\lambda)} \mathbf{I}_i \mathbf{s}_i \mathcal{P}_l^{(\lambda)}$$

with  $\mathbf{I}_i$  and  $\mathbf{s}_i$  denoting the orbital angular momentum and spin operator of the  $i$ th electron. The difference  $\Delta V_{SO,l}^{(\lambda)}$  of the radial parts of the two-component relativistic pseudopotentials

$V_{PP,l,l+1/2}^{(\lambda)}$  and  $V_{PP,l,l-1/2}^{(\lambda)}$  is written—similarly to the radial part of the spin-orbit averaged pseudopotential—in terms of Gaussian functions:

$$\Delta V_{SO,l}^{(\lambda)}(r_{i\lambda}) = \sum_k \Delta B_{lk}^{(\lambda)} \exp(-\beta_{lk}^{(\lambda)} r_{i\lambda}^2).$$

The exponential parameters  $\beta_{lk}^{(\lambda)}$  of the above ansatz are set equal to the exponential parameters of the spin-orbit averaged relativistic pseudopotentials, so that only the linear parameters  $\Delta B_{lk}^{(\lambda)}$  constitute the adjustable parameters, which are optimized in a least-squares sense to reproduce reference spin-orbit splittings derived from all-electron calculations. The spin-orbit splittings used for the adjustment were determined through first order perturbation theory from the valence orbitals of all-electron Wood-Boring calculations for several reference states of the corresponding noble gas atom and the positively charged ion. The parameters of the spin-orbit operators for the noble gas atoms are also listed in Table I.

## C. Basis sets

It has to be emphasized that the construction of our pseudopotentials and the related spin-orbit potentials is ex-

clusively based on numerical computations. Thus we have avoided any errors caused by basis set expansions up to this point and the derived parameters are absolutely independent of any sort of basis set. For using our pseudopotentials in subsequent molecular calculations, however, appropriate Gaussian-type orbital (GTO) valence basis sets have to be generated.

The errors introduced through the use of finite basis sets should not exceed the pseudopotential errors at least at the self-consistent field (SCF) level. On the other hand, the basis sets have to be as compact as possible because the major advantage of a pseudopotential calculation in comparison with an all-electron calculation is not primarily due to the omission of the core electrons but to the concomitant significant reduction of the basis set size.

In a first step the exponential parameters of  $(6s6p)$  primitive basis sets were energy-optimized<sup>52</sup> in SCF calculations on the ground states of the noble gas atoms. In the case of the neon pseudopotentials we had to augment the basis sets to  $(7s7p)$  to achieve the same accuracy as for the other atoms. Then the most compact basis functions of  $s$  and  $p$  symmetry were contracted using the respective orbital expansion coefficients of atomic ground state calculations. The resulting  $[4s4p]$  basis sets were supplemented with an optimized  $d$  function in such a way that singles–doubles configuration interaction (CISD) calculations<sup>7</sup> on the atomic ground states using the relativistic pseudopotentials yielded maximum correlation energies. The exponential parameters and contraction coefficients of our energy-optimized  $[4s4p1d]$  valence basis sets for the nonrelativistic and relativistic noble gas pseudopotentials are listed in Tables II and III.

The binding energies of noble gas containing clusters or molecules are mainly due to dispersion effects. Therefore, a convenient basis set also has to be capable of reproducing the atomic polarizabilities. In Fig. 1 we depict the dependency of the ground state SCF dipole polarizability and the CISD correlation energy of the Xe atom on the  $d$ -function exponential parameter. In the underlying calculations we used our relativistic pseudopotential. The  $s$  and  $p$  part of the basis set were taken from Table III and completely contracted according to the orbital expansion coefficients of a ground state SCF calculation. From Fig. 1 it is obvious that a single  $d$  function is not able to simultaneously yield an acceptable dipole polarizability and correlation energy. Note that the relativistic coupled Hartree–Fock value<sup>53</sup> for the dipole polarizability is  $26.97a_0^3$ .

Extended polarization function sets were generated by optimizing the exponential parameters of  $(2d1f)$  polarization sets in CISD calculations for the atomic ground states using the relativistic pseudopotentials of Table I. The derived polarization sets were augmented with one diffuse  $d$  function in an even-tempered manner. The exponential parameters of these extended polarization function sets can be found in Table IV.

#### D. Effective core polarization potential

Due to the omission of the core electrons in pseudopotential calculations it is impossible to account for core–

TABLE II. Valence basis sets for the nonrelativistic pseudopotentials for the noble gases Ne through Xe.

Ng	$s$ Functions		$p$ Functions		$d$ Function
	Exponents	Coefficients	Exponents	Coefficients	
Ne	640.067 929	−0.005 984	157.928 756	0.007 835	2.2380
	80.741 001	−0.043 145	37.329 844	0.070 759	
	14.490 616	0.370 463	12.697 051	0.285 744	
	9.070 073	0.661 631	4.582 377	0.736 347	
	1.987 257	1.000 000	1.733 935	1.000 000	
	0.806 523	1.000 000	0.639 876	1.000 000	
Ar	0.311 222	1.000 000	0.222 110	1.000 000	0.7976
	177.971 338	0.002 406	20.782 372	0.037 376	
	12.906 070	0.059 094	3.429 772	−0.494 924	
	2.867 687	−1.039 348	1.467 741	1.351 290	
	0.683 000	1.000 000	0.654 519	1.000 000	
	0.311 308	1.000 000	0.273 494	1.000 000	
Kr	0.137 359	1.000 000	0.109 043	1.000 000	0.4878
	35.515 707	0.019 099	23.237 916	0.001 960	
	15.777 835	−0.129 572	6.686 442	0.117 753	
	6.622 406	1.099 841	2.812 498	−1.091 769	
	2.309 536	1.000 000	0.668 511	1.000 000	
	0.438 251	1.000 000	0.277 656	1.000 000	
Xe	0.167 307	1.000 000	0.107 163	1.000 000	0.3218
	6.308 741	0.116 442	2.841 870	0.326 149	
	3.674 889	−0.564 082	1.977 256	−0.754 930	
	1.553 741	1.390 428	0.418 035	1.189 235	
	0.313 238	1.000 000	0.194 719	1.000 000	
	0.141 869	1.000 000	0.092 752	1.000 000	
	0.066 966	1.000 000	0.044 707	1.000 000	

valence correlation effects as can be done in all-electron calculations—at least in principle. On the other hand, the explicit treatment of intershell correlation in all-electron calculations is extremely demanding with respect to the computational effort, in spite of the conceptually simple underlying physical mechanism, namely the dynamical polarization of the atomic cores by the valence electrons. Müller *et al.*<sup>42</sup> demonstrated that the introduction of an effective core polarization potential (CPP)

$$V_{\text{CPP}}^{(\lambda)} = -\frac{1}{2}\alpha_D^{(\lambda)}\mathbf{f}_\lambda^2$$

allows an accurate description of the core–valence correlation effect in the all-electron case. In this ansatz  $\alpha_D^{(\lambda)}$  stands for the static dipole polarizability of core  $\lambda$  and

$$\mathbf{f}_\lambda = \sum_i \frac{\mathbf{r}_{\lambda i}}{r_{\lambda i}^3} [1 - \exp(-\gamma_\lambda r_{\lambda i}^2)]^q - \sum_{\mu \neq \lambda} \frac{\mathbf{R}_{\lambda\mu}}{R_{\lambda\mu}^3} \times Q_\mu [1 - \exp(-\gamma_\lambda R_{\lambda\mu}^2)]^q$$

for the electric field due to the valence electrons and the other cores. Fuentealba *et al.*<sup>38,39,54</sup> were the first to apply the above ansatz in connection with pseudopotentials, where the core polarization potential also simulates the static polarization of the atomic cores in molecules.

The cut-off factor for the electric field is necessary to account for the breakdown of the polarization model for valence electron positions too close to the cores. Note that the polarization operator is not a simple one-electron potential in

TABLE III. Valence basis sets for the relativistic pseudopotentials for the noble gases Ne through Xe.

Ng	<i>s</i> Functions		<i>p</i> Functions		<i>d</i> Function
	Exponents	Coefficients	Exponents	Coefficients	
Ne	612.002 437	-0.006 107	158.314 535	0.007 851	2.2380
	80.952 044	-0.042 603	37.301 128	0.071 316	
	13.864 201	0.452 196	12.705 558	0.286 392	
	8.745 526	0.579 956	4.587 087	0.735 394	
	1.992 346	1.000 000	1.735 662	1.000 000	
	0.800 803	1.000 000	0.640 553	1.000 000	
	0.307 774	1.000 000	0.222 544	1.000 000	
Ar	174.669 655	0.002 587	19.887 221	0.023 346	0.7976
	12.695 768	0.062 313	3.776 172	-0.224 621	
	2.917 834	-1.042 158	1.211 516	1.137 596	
	0.670 840	1.000 000	0.538 499	1.000 000	
	0.299 112	1.000 000	0.229 575	1.000 000	
	0.131 402	1.000 000	0.095 103	1.000 000	
Kr	35.402 961	0.020 495	23.029 085	0.005 625	0.4878
	15.665 089	-0.099 188	9.503 092	-0.075 051	
	6.247 711	1.072 051	2.842 461	1.045 689	
	2.394 246	1.000 000	0.689 293	1.000 000	
	0.453 489	1.000 000	0.285 136	1.000 000	
	0.172 158	1.000 000	0.108 782	1.000 000	
Xe	7.858 015	0.059 928	3.214 523	0.211 005	0.3218
	3.495 772	-0.649 076	1.884 944	-0.712 674	
	1.758 869	1.529 814	0.448 876	1.228 080	
	0.314 745	1.000 000	0.212 232	1.000 000	
	0.151 160	1.000 000	0.100 115	1.000 000	
	0.071 226	1.000 000	0.046 979	1.000 000	

the many-electron case but also contains electron–electron and electron–other core terms. The related multicenter integrals over Cartesian Gaussian functions have been solved by Schwerdtfeger and Silberbach<sup>55</sup> and were implemented into MOLPRO.<sup>56</sup>

Because we assume core polarization effects to be of minor influence in the case of the eightfold charged ionic cores of the noble gases, we restricted the construction of a

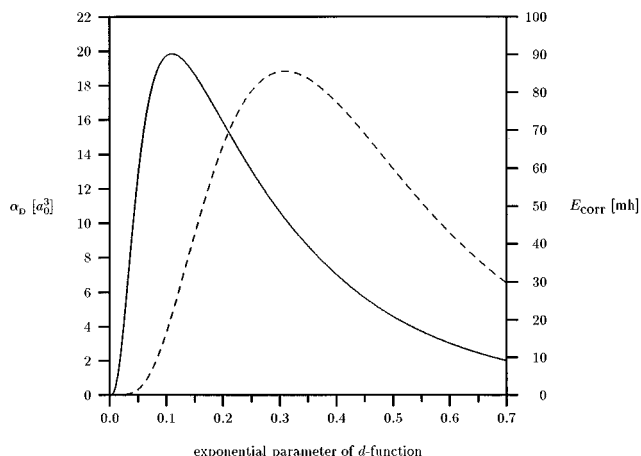


FIG. 1. SCF dipole polarizability (solid line) and CISD correlation energy (dashed line) of the Xe atom: dependency on the *d*-function exponential parameter for a  $(6s6p1d)/[1s1p1d]$  basis set, cf. the text.

TABLE IV. Extended polarization function sets for supplementing the  $[4s4p]$  basis sets of Tables II and III.

	Ne	Ar	Kr	Xe
<i>d</i> Functions	4.2748	1.4509	0.7379	0.4460
	1.1717	0.4385	0.3225	0.2322
	0.3211	0.1325	0.1409	0.1208
<i>f</i> Function	2.5795	0.9305	0.7052	0.5157

core polarization potential to the relativistic pseudopotential for xenon. The dipole polarizability of the  $\text{Xe}^{8+}$  core ( $0.8345a_0^3$ ) was taken from the tables of relativistic coupled Hartree–Fock polarizabilities by Johnson *et al.*<sup>53</sup> The exponent  $q$  of the cut-off function may be either 1 or 2. For adjusting the remaining parameter  $\gamma_\lambda$ , we first derived a single valence electron pseudopotential for the  $\text{Xe}^{8+}$  core by means of the procedure described in Sec. II A, except that the reference energies were taken from calculations on the  $\text{Xe}^{7+}$  ion instead of the neutral noble gas atom. This pseudopotential was supplemented with the effective core polarization potential and the parameter  $\gamma_\lambda$  was optimized to reproduce the experimental ionization energy of the  $\text{Xe}^{7+}$  ion (3.894 32 a.u.<sup>57</sup>).

For  $q=1$  we found the optimum cut-off parameter to be 0.973 91; further we changed the contraction coefficients of the xenon basis set of Table III when used in connection with the core polarization potential. The new contraction coefficients are 0.026 259,  $-0.298 858$ , 0.715 551 for the *s* function and 0.066 935,  $-0.229 500$ , 0.410 574 for the *p* function. For  $q=2$  the optimum cut-off parameter amounts to 1.447 08 and the modified contraction coefficients are 0.026 726,  $-0.300 866$ , 0.717 620 and 0.067 556,  $-0.230 769$ , 0.411 452 for *s* and *p* function, respectively.

### III. ATOMIC TEST CALCULATIONS

#### A. Ionization potentials and excitation energies

In Sec. II we described the generation of nonrelativistic and relativistic *ab initio* pseudopotentials as well as the optimization of corresponding valence basis sets. To demonstrate the accuracy of these pseudopotentials we list in Table V the valence energies of selected states of the noble gases Ne through Xe determined (a) in nonrelativistic and relativistic numerical all-electron Hartree–Fock (HF) calculations, (b) numerical HF, and (c) finite basis set SCF calculations using these pseudopotentials. The last two columns of this table display the pseudopotential and the basis set error (in eV) at the SCF level. It can be seen that the pseudopotential error is usually of the order of 0.02 eV and in all cases less than 0.1 eV. (In the case of Xe the  $5s^15p^6$  state was not among the reference states of the pseudopotential adjustment.) The basis set errors do not exceed 0.03 eV in any case.

Further test calculations incorporate valence correlation effects and comparison with experimental data is possible therefore. As in Table V we restrict our attention to the ground states of the neutral atoms and the  $ns^2np^5$   $^2P$  and  $ns^1np^6$   $^2S$  states of the cations, because the  $[4s4p3d1f]$

TABLE V. Comparison of the valence SCF energies (in atomic units) obtained in numerical all-electron calculations  $E_{AE}^{num}$ , numerical pseudopotential calculations  $E_{PP}^{num}$ , and analytic pseudopotential calculations  $E_{PP}^{BS}$ .  $\Delta E_{PP}$  and  $\Delta E_{BS}$  denote the pseudopotential and the basis set error (in eV) for the nonrelativistic (HF) and the relativistic (WB) pseudopotentials for the noble gas atoms.

Valence state			PP	$E_{AE}^{num}$	$E_{PP}^{num}$	$E_{PP}^{BS}$	$\Delta E_{PP}$	$\Delta E_{BS}$
Ne <sup>0</sup>	$2s^2 2p^6$	$^1S$	HF	-34.685 985	-34.685 316	-34.684 442	0.0182	0.0238
			WB	-34.709 465	-34.708 785	-34.707 908	0.0185	0.0239
Ne <sup>+</sup>	$2s^2 2p^5$	$^2P$	HF	-33.956 701	-33.956 878	-33.955 949	-0.0048	0.0253
			WB	-33.980 742	-33.980 914	-33.979 984	-0.0047	0.0253
Ne <sup>+</sup>	$2s^1 2p^6$	$^2S$	HF	-32.873 707	-32.873 625	-32.872 650	0.0022	0.0265
			WB	-32.892 781	-32.892 694	-32.891 718	0.0024	0.0266
Ar <sup>0</sup>	$3s^2 3p^6$	$^1S$	HF	-20.849 422	-20.849 867	-20.849 565	-0.0121	0.0082
			WB	-20.884 134	-20.884 584	-20.884 271	-0.0122	0.0085
Ar <sup>+</sup>	$3s^2 3p^5$	$^2P$	HF	-20.306 444	-20.306 195	-20.305 850	0.0068	0.0094
			WB	-20.341 801	-20.341 538	-20.341 172	0.0072	0.0100
Ar <sup>+</sup>	$3s^1 3p^6$	$^2S$	HF	-19.629 644	-19.629 522	-19.629 027	0.0033	0.0135
			WB	-19.656 119	-19.655 979	-19.655 459	0.0038	0.0141
Kr <sup>0</sup>	$4s^2 4p^6$	$^1S$	HF	-17.979 765	-17.980 392	-17.980 180	-0.0171	0.0058
			WB	-18.128 919	-18.129 512	-18.129 226	-0.0161	0.0078
Kr <sup>+</sup>	$4s^2 4p^5$	$^2P$	HF	-17.492 182	-17.491 919	-17.491 525	0.0072	0.0107
			WB	-17.642 558	-17.642 241	-17.641 751	0.0086	0.0133
Kr <sup>+</sup>	$4s^1 4p^6$	$^2S$	HF	-16.873 040	-16.873 029	-16.872 713	0.0003	0.0086
			WB	-16.989 697	-16.989 689	-16.989 274	0.0002	0.0113
Xe <sup>0</sup>	$5s^2 5p^6$	$^1S$	HF	-14.988 348	-14.989 100	-14.988 950	-0.0205	0.0041
			WB	-15.276 222	-15.277 055	-15.276 698	-0.0227	0.0097
Xe <sup>+</sup>	$5s^2 5p^5$	$^2P$	HF	-14.558 931	-14.558 755	-14.558 046	0.0048	0.0193
			WB	-14.848 290	-14.848 118	-14.847 369	0.0047	0.0204
Xe <sup>+</sup>	$5s^1 5p^6$	$^2S$	HF	-14.078 431	-14.075 692	-14.074 635	0.0745	0.0288
			WB	-14.303 595	-14.300 697	-14.299 664	0.0789	0.0281

basis sets used for this investigation are not capable of accurately describing excitations to the  $(n+1)$  shell or into  $d$  orbitals. With the valence energies of these states at hand we can determine the ionization potentials of the noble gases and  $ns^2 np^5 \ ^2P \rightarrow ns^1 np^6 \ ^2S$  excitation energies of the noble gas cations and compare these with the respective experimental values.

For all calculations of this section we used the quantum chemistry program package MOLPRO.<sup>7,58–62</sup> Because the molecular symmetry groups that can be treated by this program system are restricted to the Abelian group  $D_{2h}$  and its subgroups, we performed the atomic calculations in the point

group  $D_{2h}$  instead of the spherical group. In order to avoid symmetry breaking we used state-averaged multiconfiguration self-consistent field (MCSCF) calculations with three determinants for the  $^2P$  states of the cations. The ground states of the neutral atoms and the  $^2S$  states of the cations were treated at the single-determinant SCF level. Both calculations are labeled SCF in Tables VI and VII. To account for electron correlation effects we did single-reference configuration interaction with single and double excitations (CISD) and coupled electron pair (CEPA1,CEPA2) calculations. With our  $[4s4p3d1f]$  basis sets this leads to 1300–

TABLE VI. Ionization energies  $ns^2 np^6 \ ^1S \rightarrow ns^2 np^5 \ ^2P$  (in eV) of the noble gases Ne, Ar, Kr, and Xe from calculations with nonrelativistic (HF) and relativistic (WB) *ab initio* pseudopotentials in comparison with experimental data (Ref. 64).

	Ne		Ar		Kr		Xe	
	HF	WB	HF	WB	HF	WB	HF	WB
SCF	19.823	19.807	14.795	14.778	13.297	13.265	11.725	11.683
CISD	21.216	21.203	15.446	15.434	13.852	13.836	12.137	12.127
CISD+Q	21.306	21.294	15.508	15.497	13.907	13.892	12.175	12.171
CEPA1	21.291	21.279	15.505	15.493	13.904	13.889	12.175	12.170
CEPA2	21.312	21.300	15.522	15.510	13.918	13.903	12.185	12.182
CASSCF	19.771	19.756	14.814	14.800	13.387	13.368	11.818	11.796
MRCI	21.245	21.233	15.502	15.491	13.907	13.892	12.183	12.179
MRCI+Q	21.319	21.307	15.541	15.526	13.932	13.918	12.199	12.197
Reference <sup>a</sup>		21.597		15.819		14.222		12.565

<sup>a</sup>Spin-orbit averaged.

TABLE VII. Excitation energies  $ns^2np^5\ ^2P \rightarrow ns^1np^6\ ^2S$  (in eV) of the noble gas ions Ne<sup>+</sup>, Ar<sup>+</sup>, Kr<sup>+</sup>, and Xe<sup>+</sup> from calculations with nonrelativistic (HF) and relativistic (WB) *ab initio* pseudopotentials in comparison with experimental data (Ref. 64).

	Ne		Ar		Kr		Xe	
	HF	WB	HF	WB	HF	WB	HF	WB
SCF	29.478	29.613	18.417	18.659	16.839	17.755	13.154	14.904
CISD	27.003	27.126	14.760	14.962	13.711	14.497	10.597	12.019
CISD+Q	26.590	26.708	12.975	13.136	12.069	12.698	9.222	10.276
CEPA1	26.651	26.769	12.462	12.583	11.397	11.802	8.674	...
CEPA2	26.504	26.618	10.680	10.695	...	...	...	...
CASSCF	27.344	27.468	13.295	13.476	12.433	13.186	9.398	10.717
MRCI	26.689	26.808	13.301	13.474	12.373	13.077	9.421	10.645
MRCI+Q	26.597	26.714	13.280	13.456	12.355	13.054	9.415	10.628
Reference <sup>a</sup>		26.897		13.421		13.292		10.832

<sup>a</sup>Spin-orbit averaged.

2200 determinants. Size extensivity corrected CISD values<sup>63</sup> are also included in our tables (label: +Q).

Further, we performed complete active space SCF (CASSCF) calculations with the valence *s* and *p* orbitals plus a complete *d* shell constituting the active space; the respective CI expansions consisted of about 800 determinants. In the case of the <sup>2</sup>*P* states the average was taken again over the different spatial orientations of the partially occupied *p* orbitals. Finally, the orbitals of these CASSCF calculations were used in internally contracted multireference CI (MRCI) calculations.<sup>60,61</sup> All determinants of the CASSCF wave function with coefficients greater than 0.01 were used as reference configurations in the subsequent MRCI calculation leading to 30–150 reference configurations, 11 000–22 000 contracted configurations, and up to 150 000 determinants. Corresponding size extensivity corrected energy values were also determined.

The results of these calculations are summarized in Tables VI and VII together with corresponding experimental values.<sup>64</sup>

### 1. Ionization potentials

Table VI gives an overview over the ionization potentials of the noble gases calculated with our nonrelativistic (HF) and relativistic (WB) pseudopotentials at various levels of correlation treatment. The last line of the table displays the spin-orbit averaged experimental ionization potentials.<sup>64</sup> Note that the differential relativistic effects are in all cases smaller than 0.05 eV, in spite of the fact that the valence energies (cf. Table V) calculated with nonrelativistic and relativistic pseudopotentials differ significantly, with the relativistic effect increasing from Ne (0.6 eV) and Ar (1.0 eV) to Kr (4.0 eV) and Xe (7.8 eV). The ionization potentials determined with the nonrelativistic pseudopotentials are in all cases greater than the respective values obtained with the relativistic pseudopotentials. The energy differences exhibited by calculations at the correlated level are even smaller than those from SCF calculations.

Much more important than scalar relativistic effects is the incorporation of electron correlation, which contributes between 0.5 (Xe) and 1.5 eV (Ne) to the ionization potentials. The CISD method proves to be already a reliable ap-

proximation. Size extensivity corrections are smaller than 0.1 eV and the MRCI values do not constitute significant improvements.

In comparison with the experimental ionization potentials the calculated values are systematically too small by 0.3 eV (1.3%–3.0%). Taking into account the importance of the differential correlation effect we believe that the deviations are due to the incomplete one-particle basis sets. All-electron calculations for neon and argon with basis sets comparable to the valence basis sets used in our investigations also exhibit errors of the order of 0.3 eV, which are reduced to 0.1 eV when the basis sets are augmented to [*6s5p4d3f2g1h*] (Ne) and [*7s6p4d3f2g1h*] (Ar).<sup>65–67</sup>

### 2. Excitation energies

In contrast to the ionization potentials discussed in the last paragraph the  $ns^2np^5\ ^2P \rightarrow ns^1np^6\ ^2S$  excitation energies of the noble gas cations are significantly influenced by scalar relativistic effects (cf. Table VII). The relativistic stabilization of the *s* orbitals leads to an increase of the excitation energies, especially for Kr (0.7 eV) and Xe (1.2 eV). Similar to the ionization potentials relativistic and correlation effects are not simply additive: The influence of relativity at the SCF level is by 50% higher than that exhibited in the CASSCF/MRCI calculations.

Though the importance of relativistic effects has increased in comparison to the first ionization potentials, the valence correlation effects still constitute the most important contributions to the excitation energies (Ne: 2.9 eV; Ar: 5.2 eV; Kr: 4.7 eV; Xe: 4.3 eV). Except for the case of the Ne atom single-reference methods seem to be completely inappropriate to describe this excitation energy: Indications are the large size extensivity corrections of up to 1.8 eV and the difficulties with the CEPA method, which did not converge for Kr and Xe. On the other hand, the excitation energies obtained in CASSCF/MRCI calculations differ from the respective spin-orbit averaged experimental data<sup>64</sup> by 0.2 eV only. This enormous effect of electron correlation seems to be a quasidegeneracy effect.

TABLE VIII. Spin-orbit splittings (in eV) of the  $ns^2np^5\ ^2P$  states of the noble gas cations  $\text{Ne}^+$ ,  $\text{Ar}^+$ ,  $\text{Kr}^+$ , and  $\text{Xe}^+$  from pseudopotential calculations in comparison with all-electron Dirac-Fock (DF) calculations and experimental data (Ref. 64).

	$\text{Ne}^+$	$\text{Ar}^+$	$\text{Kr}^+$	$\text{Xe}^+$
SCF	0.116	0.179	0.645	1.242
CIS	0.114	0.175	0.635	1.225
CISD <sup>a</sup>	0.114	0.173	0.628	1.208
CISD <sup>b</sup>	0.114	0.173	0.627	1.203
AE, DF	0.103	0.187	0.680	1.336
Expt.	0.097	0.178	0.666	1.307

<sup>a</sup>Maximum number of unpaired electrons: 3.

<sup>b</sup>Maximum number of unpaired electrons: 5.

## B. Spin-orbit splittings

In order to test the reliability of our spin-orbit operators we investigated the spin-orbit splittings of the  $ns^2np^5\ ^2P$  states of the noble gas cations in two-component calculations using the relativistic averaged *ab initio* pseudopotentials, the corresponding spin-orbit operators, and  $[4s4p3d]$  valence basis sets, thus omitting the *f* functions. All calculations of this section were done within the intermediate coupling scheme with the double group configuration interaction (DGCI) program package of Pitzer *et al.*<sup>51,68</sup>

The procedure for obtaining spin-orbit splittings with this program is as follows: First of all one does a scalar SCF calculation to gain the orbitals needed to generate the determinants, which constitute the many-particle basis set of the subsequent configuration interaction calculation. Then the Hamiltonian is augmented by the spin-orbit operator, the CI matrix is constructed and finally diagonalized. The resulting spin-orbit splittings for the ground states of the noble gas cations are listed in Table VIII.

The line labeled SCF in Table VIII thus shows perturbation theoretical spin-orbit splittings which deviate from splittings determined in numerical averaged-level Dirac-Fock (DF) calculations<sup>69</sup> by 4%–12%. Inclusion of singly and doubly excited determinants leads to a slight decrease of the calculated spin-orbit splittings which is in accordance with the difference between the Dirac-Fock values and the experimentally determined splittings.<sup>64</sup>

## IV. ATOMIC DIPOLE AND QUADRUPOLE POLARIZABILITIES

As already mentioned in connection with the construction of the valence basis sets for the pseudopotentials, the bonding in clusters or molecules containing noble gas atoms is mainly due to dispersion effects. Therefore, the atomic dipole polarizability constitutes a reasonable criterion to judge the quality of a basis set for noble gas atoms.

We used the finite-field method to calculate the ground state dipole polarizabilities with our nonrelativistic and relativistic pseudopotentials and the corresponding  $[4s4p3d1f]$  basis sets. We performed SCF as well as several single-reference correlated level calculations with the program package MOLPRO.<sup>7,58–62</sup> We applied a homogeneous static electric field of strength  $f=0.010$  a.u. Reduction of the field strength to  $f=0.001$  a.u. did not significantly affect the po-

TABLE IX. Dipole polarizabilities (in  $a_0^3$ ) of the noble gases Ne, Ar, Kr, and Xe from calculations with nonrelativistic (HF) and relativistic (WB) *ab initio* pseudopotentials in comparison with all-electron SCF (Ref. 70) (AE-SCF), relativistic coupled Hartree-Fock (Ref. 53) (RCHF), and experimental values.

	Ne		Ar		Kr		Xe	
	HF	WB	HF	WB	HF	WB	HF	WB
SCF	2.078	2.084	10.243	10.300	14.314	14.152	26.011	25.732
CISD	2.210	2.217	10.363	10.426	14.303	14.154	26.062	25.841
CISD+Q	2.234	2.241	10.427	10.492	14.344	14.196	26.197	25.969
CEPA1	2.231	2.238	10.426	10.491	14.343	14.195	26.178	25.966
CEPA2	2.237	2.244	10.446	10.512	14.357	14.209	26.219	26.011
AE-SCF	2.377		10.757		16.477		27.100	
RCHF		2.380		10.770		16.470		26.970
Expt. <sup>a</sup>		2.669		11.08		16.79		27.16
Expt. <sup>b</sup>		2.678		11.221		17.075		27.815

<sup>a</sup>Reference 71.

<sup>b</sup>Reference 72.

larizabilities but increased the numerical uncertainties. In Table IX we compare our pseudopotential results with polarizabilities from an SCF investigation using extended basis sets.<sup>70</sup> Relativistic coupled Hartree-Fock<sup>53</sup> and experimental values<sup>71,72</sup> are also included. Note that the polarizabilities derived with the pseudopotentials amount to 85% (Ne,Kr) and 95% (Ar,Xe) of the corresponding reference values. Thus the derived basis sets are able to describe the dipole polarizabilities of the noble gas atoms in a satisfactory way.

To determine more accurate values of the static dipole and quadrupole polarizabilities we augmented our valence basis sets with two diffuse *s* and *p* functions with the exponential parameters (0.124, 0.050; 0.089, 0.036) for neon, (0.054, 0.021; 0.041, 0.016) for argon, (0.068, 0.027; 0.043, 0.017) for krypton, and (0.028, 0.011; 0.018, 0.007) for xenon. We dropped the  $(3d1f)$  part and supplemented the resulting  $(8s8p)/[6s6p]$  basis sets [in the case of neon  $(9s9p)/[6s6p]$ ] with  $(6d6f)$  polarization function sets. As exponential parameters of these *d* and *f* functions we chose the exponents of the six most diffuse primitive functions of the respective *p* set. We omitted *g* and higher angular momentum functions because diffuse functions have been proven to be more important than *g* functions.<sup>67,73</sup>

With these extended basis sets we did finite-field calculations on the static dipole polarizabilities of the noble gas atoms using field strengths of 0.001, 0.002, 0.005, 0.010, and 0.020 a.u. at the SCF, second-order Møller-Plesset perturbation theory (MP2), CCSD, and CCSD with perturbational inclusion of triple excitations [CCSD(T)] levels of theory. The dipole polarizabilities displayed in Table X were derived by extrapolation to zero field strength, thus removing hyperpolarizability effects. To determine static quadrupole polarizabilities we used an arrangement of point charges on the *z* axis at coordinates  $2R$ ,  $R$ ,  $-R$ , and  $-2R$  with charges  $-32Q$ ,  $Q$ ,  $Q$ , and  $-32Q$ , respectively, as suggested by Maroulis and Thakkar.<sup>74</sup> The quadrupole polarizability  $\alpha_Q$  is obtained from the formula

$$\alpha_Q \approx [2E(0) - E(Q) - E(-Q)] \frac{R^6}{36Q^2},$$



TABLE X. Dipole and quadrupole polarizabilities (in  $a_0^3$  and  $a_0^5$ , respectively) of the noble gases Ne, Ar, Kr, and Xe from calculations with nonrelativistic (HF) and relativistic (WB) *ab initio* pseudopotentials and extended  $[6s6p6d6f]$  valence basis sets in comparison with all-electron SCF (Ref. 70) (AE-SCF), relativistic coupled Hartree–Fock (Ref. 53) (RCHF), and experimental values where available.

	Ne		Ar		Kr		Xe	
	HF	WB	HF	WB	HF	WB	HF	WB
Dipole polarizabilities $\alpha_D$								
SCF	2.372	2.375	10.603	10.593	16.434	16.405	26.936	26.682
MP2	2.710	2.714	11.029	11.032	16.976	16.966	27.623	27.417
CCSD	2.641	2.645	10.974	10.974	16.955	16.942	27.711	27.493
CCSD(T)	2.689	2.693	11.072	11.073	17.075	17.064	27.869	27.658
AE-SCF	2.377		10.757		16.477		27.100	
RCHF		2.38		10.77		16.47		26.97
Expt. <sup>a</sup>		2.669		11.08		16.79		27.16
Expt. <sup>b</sup>		2.678		11.221		17.075		27.815
Quadrupole polarizabilities $\alpha_Q$								
SCF	6.41	6.41	49.63	49.54	95.22	93.55	211.47	201.66
MP2	7.64	7.64	52.13	52.09	98.71	97.14	216.72	207.30
CCSD	7.35	7.35	51.73	51.66	98.21	96.57	218.26	208.35
CCSD(T)	7.52	7.52	52.32	52.25	99.04	97.39	219.78	209.85
AE-SCF	6.42		50.19		95.50		212.60	
RCHF		6.43		50.12		94.25		204.3

<sup>a</sup>Reference 71.

<sup>b</sup>Reference 72.

in which  $E(Q)$  denotes the energy of the atom in the quadrupolar field. This special arrangement not only avoids contributions from “odd” terms involving  $f_z, f_{zzz}, \dots$ , but also the hexadecapolar terms involving  $f_{zzzz}$ . The combination of  $E(Q)$  and  $E(-Q)$  eliminates all terms involving odd powers of the “even” gradients. We chose the parameters to be  $R=22a_0$ ,  $Q=4$  in the case of neon and argon, and  $R=22a_0$ ,  $Q=2$  for krypton and xenon, leading to field gradients of 0.004 508 and 0.002 254 a.u. The results of SCF, MP2, CCSD, and CCSD(T) calculations on the static quadrupole polarizabilities of the noble gas atoms are listed in Table X together with other theoretically determined values.<sup>53,70</sup>

Our SCF dipole polarizabilities can be compared with corresponding values from Bishop and Cybulski,<sup>70</sup> who used extended basis sets in their all-electron SCF calculations (AE-SCF in Table X), and the relativistic coupled Hartree–Fock values of Johnson *et al.*<sup>53</sup> (labeled RCHF). The deviations from these values are in most cases smaller than 0.5%. Comparison of our SCF quadrupole polarizabilities with the corresponding values of the same authors exhibits deviations of approximately 1%. Thus our one-particle basis sets are nearly complete. The relativistic effects determined by comparison of the calculations with nonrelativistic and relativistic pseudopotentials are in line with the relativistic effects derived from the cited all-electron calculations.

Inclusion of electron correlation increases the dipole and quadrupole polarizabilities as can be seen from CCSD calculations. A further increase occurs when triple contributions are taken into account. The total contributions of correlation to the dipole polarizabilities of the noble gases are (triple contributions in parentheses) +11.8% (+1.8%) for neon, +4.3% (+0.9%) for argon, +3.9% (+0.7%) for krypton, and +3.5% (+0.6%) for xenon. The respective contributions to the quadrupole polarizabilities are +14.8% (+2.3%) for

neon, +5.2% (+1.1%) for argon, +3.9% (+0.8%) for krypton, and +3.9% (+0.7%) for xenon. To allow a simple comparison with the influence of scalar relativistic effects we give the corresponding relativistic contributions to the dipole (quadrupole) polarizabilities:  $-0.1\%$  ( $-1.7\%$ ) for krypton and  $-0.8\%$  ( $-4.7\%$ ) for xenon, while relativity is negligible for neon and argon. Thus relativity overrides the correlation effect in the case of the quadrupole polarizability of the xenon atom.

To investigate the influence of core–valence correlation we repeated the relativistic pseudopotential calculations for xenon incorporating the effective core polarization potential (CPP). At the CCSD(T) level we get a dipole polarizability of  $27.317a_0^3$  and a quadrupole polarizability of  $205.50a_0^5$ . Thus we observe a reduction of the dipole (quadrupole) polarizability by 1.2% (2.1%) through core–valence correlation.

In recent years there have been several publications on the dipole and quadrupole polarizabilities of the noble gases by different groups.<sup>67,73–77</sup> Rice *et al.*<sup>73,77</sup> published a conscientious investigation of the dipole polarizabilities of the noble gases Ne to Xe, using atomic natural orbital (ANO) basis sets augmented by diffuse functions in all-electron calculations up to the CCSD(T) level. Their CCSD(T) values (Ne:  $2.69a_0^3$ ; Ar:  $11.21a_0^3$ ; Kr:  $17.16a_0^3$ ; Xe:  $27.99a_0^3$ ) are in excellent agreement with our nonrelativistic pseudopotential CCSD(T) data (cf. Table X). Their estimations of the influence of relativity and core–valence correlation are in line with our findings. Furthermore, they give a value for the quadrupole polarizability of neon<sup>73</sup> which is identical to our result. Chong and Langhoff<sup>76</sup> determined the dipole polarizability of neon using extended all-electron basis sets and CCSD(T) level of theory. Their value of  $2.684a_0^3$  is in perfect agreement with our CCSD(T) result.

Woon and Dunning<sup>67</sup> used so-called correlation-

consistent basis sets, which they augmented with diffuse basis functions, in order to extrapolate to the basis set limit. They give all-electron values of dipole and quadrupole polarizabilities of neon and argon for several levels of correlation treatment up to CCSD(T). Their extrapolated CCSD(T) dipole (quadrupole) polarizabilities are  $2.680a_0^3$  ( $7.52a_0^5$ ) for neon and  $11.12a_0^3$  ( $52.8a_0^5$ ) for argon. Our pseudopotential results are in excellent agreement with these data.

Maroulis and Thakkar<sup>74,75</sup> published CCD(ST) values of the dipole and quadrupole polarizability of neon as well as SDQ-MP4 values of the dipole and quadrupole polarizabilities of krypton and xenon using extended all-electron basis sets. Their values are (quadrupole polarizabilities in parentheses)  $2.698a_0^3$  ( $7.525a_0^5$ ) for neon,  $17.08a_0^3$  ( $99.86a_0^5$ ) for krypton, and  $27.76a_0^3$  ( $216.5a_0^5$ ) for xenon, in near-perfect agreement with our nonrelativistic pseudopotential CCSD(T) results. We suppose the small deviation in the case of xenon to be due to deficiencies of their ( $17s14p10d4f$ )/[ $12s11p8d4f$ ] basis set.

The agreement of our relativistic pseudopotential CCSD(T) dipole polarizabilities with the corresponding experimental data<sup>71,72</sup> is convenient. Assuming that extension of the basis sets would increase the dipole polarizabilities, we suppose the recent values of Hohm and Kerl<sup>72</sup> to be superior to those of Kumar and Meath.<sup>71</sup>

## V. CONCLUSIONS

Nonrelativistic and scalar relativistic energy-adjusted *ab initio* pseudopotentials substituting the  $\text{Ng}^{8+}$  cores of the noble gases neon through argon are presented together with spin-orbit potentials supplementing the one-component relativistic pseudopotentials. A semiempirical effective core polarization potential to account for core-valence correlation effects has been derived for xenon. Accurate valence basis sets including extended polarization function sets have been optimized. Atomic test calculations on ionization potentials, excitation energies, spin-orbit splittings, and dipole polarizabilities exhibit the reliability of the devised pseudopotentials and valence basis sets in comparison with all-electron calculations as well as experimental data. It is demonstrated that the extended polarization function sets of ( $3d1f$ ) size account for 85%–95% of the atomic dipole polarizability and their use instead of a single  $d$  function is recommended where tractable.

Together with augmented valence basis sets we have used the presented pseudopotentials in an investigation on the static dipole and quadrupole polarizabilities of the noble gas atoms neon through xenon in their ground states. The comparison of results from nonrelativistic and relativistic pseudopotential calculations allows the determination of relativistic effects at the CCSD(T) level of theory without resorting to perturbation theory. Relativity proves to be significant for krypton and xenon. The influence of valence electron correlation, that has been investigated by means of MP2, CCSD, and CCSD(T) calculations, decreases from neon to xenon. Core-valence correlation has been assessed using the effective core polarization potential and proves to be non-negligible in the case of xenon. Our pseudopotential

derived values for the dipole and quadrupole polarizabilities of the noble gas atoms prove to be as reliable as corresponding all-electron data published recently.

## ACKNOWLEDGMENTS

We are grateful to Professor H.-J. Werner, Universität Stuttgart, for providing the program package MOLPRO. Thanks are due to Professor R. M. Pitzer, Ohio State University, Columbus, for supplying his double group CI program. The financial support of the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

- <sup>1</sup>J. D. Weeks, A. Hazi, and S. A. Rice, *Adv. Chem. Phys.* **16**, 283 (1969).
- <sup>2</sup>J. N. Bardsley, *Case Stud. At. Phys.* **4**, 299 (1974).
- <sup>3</sup>M. Krauss and W. J. Stevens, *Annu. Rev. Phys. Chem.* **35**, 357 (1984).
- <sup>4</sup>R. Shepard, I. Shavitt, R. M. Pitzer, D. C. Comeau, M. Pepper, H. Lischka, P. G. Szalay, R. Ahlrichs, F. B. Brown, and J.-G. Zhao, *Int. J. Quantum Chem., Quantum Chem. Symp.* **22**, 149 (1988).
- <sup>5</sup>M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, Jr., *J. Comput. Chem.* **14**, 1347 (1993).
- <sup>6</sup>GAUSSIAN is a package of *ab initio* programs written by M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople.
- <sup>7</sup>MOLPRO is a package of *ab initio* programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. Peterson, R. Pitzer, A. J. Stone, and P. R. Taylor.
- <sup>8</sup>R. Ahlrichs, M. Bär, M. Häser, H. Horn, and C. Kölmel, *Chem. Phys. Lett.* **162**, 165 (1989).
- <sup>9</sup>S. Huzinaga, M. Klobukowski, and Y. Sakai, *J. Phys. C* **88**, 4880 (1984).
- <sup>10</sup>Z. Barandiarán, L. Seijo, and S. Huzinaga, *J. Chem. Phys.* **93**, 5843 (1990).
- <sup>11</sup>Z. Barandiarán and L. Seijo, *Can. J. Chem.* **70**, 409 (1992).
- <sup>12</sup>P. Durand and J. C. Barthelat, *Theor. Chim. Acta* **38**, 283 (1975).
- <sup>13</sup>P. A. Christiansen, Y. S. Lee, and K. S. Pitzer, *J. Chem. Phys.* **71**, 4445 (1979).
- <sup>14</sup>P. J. Hay and W. R. Wadt, *J. Chem. Phys.* **82**, 270 (1985).
- <sup>15</sup>W. R. Wadt and P. J. Hay, *J. Chem. Phys.* **82**, 284 (1985).
- <sup>16</sup>P. J. Hay and W. R. Wadt, *J. Chem. Phys.* **82**, 299 (1985).
- <sup>17</sup>L. F. Pacios and P. A. Christiansen, *J. Chem. Phys.* **82**, 2664 (1985).
- <sup>18</sup>M. M. Hurley, L. F. Pacios, P. A. Christiansen, R. B. Ross, and W. C. Ermler, *J. Chem. Phys.* **84**, 6840 (1986).
- <sup>19</sup>L. A. LaJohn, P. A. Christiansen, R. B. Ross, T. Atashroo, and W. C. Ermler, *J. Chem. Phys.* **87**, 2812 (1987).
- <sup>20</sup>W. C. Ermler, R. B. Ross, and P. A. Christiansen, *Int. J. Quantum Chem.* **40**, 829 (1991).
- <sup>21</sup>R. B. Ross, S. Gayen, and W. C. Ermler, *J. Chem. Phys.* **100**, 8145 (1994).
- <sup>22</sup>W. J. Stevens, H. Basch, and M. Krauss, *J. Chem. Phys.* **81**, 6026 (1984).
- <sup>23</sup>W. J. Stevens, M. Krauss, H. Basch, and P. G. Jasien, *Can. J. Chem.* **70**, 612 (1992).
- <sup>24</sup>T. R. Cundari and W. J. Stevens, *J. Chem. Phys.* **98**, 5555 (1993).
- <sup>25</sup>J. C. Barthelat, P. Durand, and A. Serafini, *Mol. Phys.* **33**, 159 (1977).
- <sup>26</sup>U. Wedig, M. Dolg, H. Stoll, and H. Preuss, in *The Challenge of Transition Metals and Coordination Chemistry*, edited by A. Veillard (Reidel, Dordrecht, 1986), pp. 79–89.
- <sup>27</sup>M. Dolg, U. Wedig, H. Stoll, and H. Preuss, *J. Chem. Phys.* **86**, 866 (1987).
- <sup>28</sup>W. Küchle, M. Dolg, H. Stoll, and H. Preuss, *Mol. Phys.* **74**, 1245 (1991).
- <sup>29</sup>A. Bergner, M. Dolg, W. Küchle, H. Stoll, and H. Preuss, *Mol. Phys.* **80**, 1431 (1993).
- <sup>30</sup>M. Dolg, H. Stoll, A. Savin, and H. Preuss, *Theor. Chim. Acta* **75**, 173 (1989).
- <sup>31</sup>M. Dolg, H. Stoll, and H. Preuss, *J. Chem. Phys.* **90**, 1730 (1989).
- <sup>32</sup>D. Andrae, U. Häussermann, M. Dolg, H. Stoll, and H. Preuss, *Theor. Chim. Acta* **77**, 123 (1990).
- <sup>33</sup>W. Küchle, M. Dolg, H. Stoll, and H. Preuss, *J. Chem. Phys.* **100**, 7535 (1994).

- <sup>34</sup>M. Dolg, H. Stoll, H. Preuss, and R. M. Pitzer, *J. Phys. Chem.* **97**, 5852 (1993).
- <sup>35</sup>U. Häussermann, M. Dolg, H. Stoll, H. Preuss, P. Schwerdtfeger, and R. M. Pitzer, *Mol. Phys.* **78**, 1211 (1993).
- <sup>36</sup>M. Dolg, A. Nicklass, and H. Stoll, *J. Chem. Phys.* **99**, 3614 (1993).
- <sup>37</sup>U. Steinbrenner, A. Bergner, M. Dolg, and H. Stoll, *Mol. Phys.* **82**, 3 (1994).
- <sup>38</sup>P. Fuentealba, H. Preuss, H. Stoll, and L. von Szentpály, *Chem. Phys. Lett.* **89**, 418 (1982).
- <sup>39</sup>L. von Szentpály, P. Fuentealba, H. Preuss, and H. Stoll, *Chem. Phys. Lett.* **93**, 555 (1982); **95**, 617(E) (1983).
- <sup>40</sup>P. Fuentealba, L. von Szentpály, H. Preuss, and H. Stoll, *J. Phys. B* **18**, 1287 (1985).
- <sup>41</sup>G. Igel-Mann, H. Stoll, and H. Preuss, *Mol. Phys.* **65**, 1321 (1988).
- <sup>42</sup>W. Müller, J. Flesch, and W. Meyer, *J. Chem. Phys.* **80**, 3297 (1984).
- <sup>43</sup>W. Kutzelnigg and F. Schmitz, in *Unkonventionelle Wechselwirkungen in der Chemie metallischer Elemente: Bericht zum Schwerpunktprogramm "Neue Phänomene in der chemie metallischer Elemente mit abgeschlossenen inneren Elektronenzuständen" der Deutschen Forschungsgemeinschaft*, edited by B. Krebs (VCH, Weinheim, 1992), pp. 17–29.
- <sup>44</sup>M. Kaupp, P. von R. Schleyer, and H. Stoll, *J. Phys. Chem.* **96**, 9801 (1992).
- <sup>45</sup>E. Czuchaj, F. Rebentrost, H. Stoll, and H. Preuss, *Chem. Phys.* **177**, 107 (1993).
- <sup>46</sup>A. Veldkamp and G. Frenking, *Chem. Phys. Lett.* **226**, 11 (1994).
- <sup>47</sup>C. Froese Fischer, *Comput. Phys. Commun.* **14**, 145 (1978); M. Dolg, modified version for pseudopotential and relativistic calculations.
- <sup>48</sup>R. D. Cowan and D. C. Griffin, *J. Opt. Soc. Am.* **66**, 1010 (1976).
- <sup>49</sup>J. H. Wood and A. M. Boring, *Phys. Rev. B* **18**, 2701 (1978).
- <sup>50</sup>B. A. Murtagh and R. W. H. Sargent, *Comput. J.* **13**, 185 (1970).
- <sup>51</sup>R. M. Pitzer and N. W. Winter, *J. Phys. C* **92**, 3061 (1988).
- <sup>52</sup>J. C. Barthelat and P. Durand, Program PSATOM, Université Paul Sabatier, Toulouse, France (1981).
- <sup>53</sup>W. R. Johnson, D. Kolb, and K.-N. Huang, *At. Data Nucl. Data Tables* **28**, 333 (1983).
- <sup>54</sup>H. Stoll, P. Fuentealba, M. Dolg, J. Flad, L. v. Szentpály, and H. Preuss, *J. Chem. Phys.* **79**, 5532 (1983).
- <sup>55</sup>P. Schwerdtfeger and H. Silberbach, *Phys. Rev. A* **37**, 2834 (1988); **42**, 665(E) (1990).
- <sup>56</sup>A. Nicklass (unpublished work, 1994).
- <sup>57</sup>S. Bashkin, R. Hallin, J. Leavitt, U. Litzen, and D. Walker, *Phys. Scr.* **23**, 5 (1981).
- <sup>58</sup>H.-J. Werner and P. J. Knowles, *J. Chem. Phys.* **82**, 5053 (1985).
- <sup>59</sup>P. J. Knowles and H.-J. Werner, *Chem. Phys. Lett.* **115**, 259 (1985).
- <sup>60</sup>H.-J. Werner and P. J. Knowles, *J. Chem. Phys.* **89**, 5803 (1988).
- <sup>61</sup>P. J. Knowles and H.-J. Werner, *Chem. Phys. Lett.* **145**, 514 (1988).
- <sup>62</sup>C. Hampel, K. A. Peterson, and H.-J. Werner, *Chem. Phys. Lett.* **190**, 1 (1992).
- <sup>63</sup>S. R. Langhoff and E. R. Davidson, *Int. J. Quantum Chem.* **8**, 61 (1974).
- <sup>64</sup>C. E. Moore, *Atomic Energy Levels*, Nat. Bur. Stand. Circ. No. 467 (National Bureau of Standards, Washington, D.C., 1949, 1952, and 1958), Vols. I, II, and III.
- <sup>65</sup>T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
- <sup>66</sup>D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **98**, 1358 (1993).
- <sup>67</sup>D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **100**, 2975 (1994).
- <sup>68</sup>A. Chang and R. M. Pitzer, *J. Am. Chem. Soc.* **111**, 2500 (1989).
- <sup>69</sup>K. G. Dyall, I. P. Grant, C. T. Johnson, F. A. Parpia, and E. P. Plummer, *Comput. Phys. Commun.* **55**, 425 (1989).
- <sup>70</sup>D. M. Bishop and S. M. Cybulski, *Chem. Phys. Lett.* **211**, 255 (1993).
- <sup>71</sup>A. Kumar and W. J. Meath, *Can. J. Chem.* **63**, 1616 (1985).
- <sup>72</sup>U. Hohm and K. Kerl, *Mol. Phys.* **69**, 803 (1990).
- <sup>73</sup>P. R. Taylor, T. J. Lee, J. E. Rice, and J. Almlöf, *Chem. Phys. Lett.* **163**, 359 (1989).
- <sup>74</sup>G. Maroulis and A. J. Thakkar, *Chem. Phys. Lett.* **156**, 87 (1989).
- <sup>75</sup>G. Maroulis and A. J. Thakkar, *J. Chem. Phys.* **89**, 7320 (1988).
- <sup>76</sup>D. P. Chong and S. R. Langhoff, *J. Chem. Phys.* **93**, 570 (1990).
- <sup>77</sup>J. E. Rice, P. R. Taylor, T. J. Lee, and J. Almlöf, *J. Chem. Phys.* **94**, 4972 (1991).