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Multiconfiguration Dirac−Hartree−Fock Adjusted Energy-Consistent Pseudopotential for Uranium: Spin−Orbit Configuration Interaction and Fock-Space Coupled-Cluster Study of U^{4+} and U^{5+} †

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In order to assess the accuracy of a recently adjusted relativistic energy-consistent small-core pseudopotential for uranium, the U^{5+} ($5f^1$ subconfiguration) spin−orbit splitting as well as the fine structure of the U^{4+} ($5f^2$ subconfiguration) spectrum have been calculated. The pseudopotential has been adjusted to four-component all-electron data, i.e., at the multiconfiguration Dirac−Hartree−Fock level using the Dirac−Coulomb Hamiltonian with a Fermi nucleus charge distribution and perturbatively including the Breit interaction. Its performance in a dressed effective Hamiltonian spin−orbit configuration interaction framework is compared to that of an older scalar-relativistic Wood−Boring adjusted pseudopotential, supplemented by a valence spin−orbit term, as well as to all-electron calculations using the Douglas−Kroll−Hess Hamiltonian. Electron correlation is accounted for by the multireference configuration interaction method with and without the Davidson correction and with different frozen-orbital spaces. Our best calculations show satisfactory agreement with experimental data; i.e., the mean absolute (relative) deviations amount to 183 (2.4%) and 948 cm^{-1} (5.1%) for the U^{5+} and the U^{4+} fine-structure energy levels, respectively. Even better agreement, comparable to the one for rigorous highly correlated four-component all-electron data, is obtained in intermediate Hamiltonian Fock-space coupled-cluster calculations applying the new pseudopotential.

1. Introduction

The chemical investigation of uranium and its compounds involves several difficulties for both experimental and theoretical work. While the toxicity and radioactivity of uranium are the main obstacles for the experimentalists,[1] theoreticians face particular challenges in the significant contributions of relativity as well as electron correlation.[2−5] Furthermore, the nearly degenerate 5f, 6d, 7s, and 7p orbitals give rise to a multitude of possible configuration interactions and a high density of low-lying states, which complicates computations and renders assignment of experimental spectra difficult.[6]

One of the most successful approximations to cope with some of these problems in quantum chemical calculations is the pseudopotential (PP) approach, in which the explicit calculations are restricted to the chemically relevant valence electron system and relativistic effects are only implicitly accounted for by a proper adjustment of free parameters in the valence model Hamiltonian. So-called energy-consistent PPs can be designed to account for relativistic corrections at essentially any computational level, for which accurate atomic all-electron (AE) reference calculations are feasible.[7] Moreover, due to the applicability of smaller valence basis sets the PP approximation significantly reduces the computational costs compared to AE calculations.

In 1994 5f-in-valence scalar-relativistic Wood−Boring (WB) PPs[8] for actinides were generated and later on additional effective valence spin−orbit operators[9] adjusted to AE state-averaged multiconfiguration Dirac−Hartree−Fock (MCDHF) data obtained with the Dirac−Coulomb (DC) Hamiltonian were provided. These pseudopotentials have been successfully applied in many calculations but showed less satisfactory results in the case of the third and fourth ionization potentials (IPs); i.e., the finite difference PP multiconfiguration Hartree−Fock (MCHF) results deviate on an average by 0.28 (1.4%) and 0.53 eV (1.5%) from AE MCDHF values based on the Dirac−Coulomb−Breit (DCB) Hamiltonian for IP3 and IP4, respectively.[10] In the case of IP1 and IP2 these deviations amount only to 0.03 (0.6%) and 0.06 eV (0.5%), respectively, because in contrast to IP3 and IP4 these ionizations mainly take place without changes in the 5f occupation. Test calculations indicated that the large deviations for the higher IPs do not arise from the PP approximation itself but rather from the deviations between the underlying AE WB from the corresponding MCDHF/DCB average energies. Therefore, a readjustment of the PPs directly to four-component AE MCDHF/DCB reference data within the intermediate coupling scheme appears to be desirable.

Such small-core PPs, with an adjustment to valence spectra from AE MCDHF calculations, are already available for the group 1,[11] 2,[12] and post-d main group elements,[13−15] for groups 11 and 12 transition metal elements,[16] and for the 3d,[17] 4d,[18] and 5d[19] elements. Recently the adjustment of a variety of such MCDHF-based PPs has been examined for the uranium atom as a representative example for the actinide elements.[20] For reasons of comparison to the most accurate atomic AE calculations available from literature we chose for this work a MCDHF

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PP based on the Dirac−Coulomb Hamiltonian, with a Fermi nuclear charge distribution and perturbatively including the (low-frequency limit) Breit interaction (DCB).[21] Further information concerning the selection of the reference data and the adjustment of this PP can be found in a recent review article.[7] The PP has recently also been tested for uranium monohydride UH[20] and even shows an overall better performance for the spectroscopic constants of the low-lying electronic states and the ground state binding energy than the older WB PP, which already gave results quite close to those of AE calculations using the Douglas−Kroll−Hess Hamiltonian (DKH) augmented by the Breit−Pauli spin−orbit (SO) Hamiltonian.[22]

In order to further test the MCDHF/DCB PP, in this work it will be applied to calculate the fine structure of the U^{5+} and U^{4+} spectra at low energies using a two-step configuration interaction (CI) approach identical to that used by Danilo et al.,[23] i.e., a dressed effective Hamiltonian relativistic spin−orbit configuration interaction (SO-CI) scheme.[24,25] These benchmark systems were chosen, because experimental[26−28] as well as computational[6,23,29−31] reference data are available. We note that the current study covers only 2% of the configurations and 0.04% of the *J* levels of the reference data used in the PP adjustment and thus the applied PP is by no means tuned to describe these cases especially well. Electron correlation will be treated using the multireference configuration interaction (MRCI) method with and without the Davidson size-extensivity correction (DaC) and with different frozen-orbital spaces. The best choice of the SO-CI configuration space is investigated in the case of the U^{5+} SO splitting. In addition results of intermediate Hamiltonian Fock-space coupled-cluster (IH-FSCC) PP calculations using the approach of Kaldor and co-workers[32,33] will be reported.

2. Method

The pseudopotential and basis set used in this contribution were previously published and discussed in detail elsewhere[7,20] and will be described here only briefly. The new 5f-in-valence PP corresponding to uranium treats 32 valence electrons explicitly, while the 1s−4f shells (60 electrons) are included in the PP core. The PP parameters up to f symmetry were adjusted to four-component AE MCDHF/DCB reference data,[21] which comprised 100 nonrelativistic configurations yielding a total of 30190 *J* levels. The reference data were obtained for $U-U^{7+}$ and included a wide spectrum of occupations in the 5f, 6d, 7s, and 7p valence shells, but also additional configurations with holes in the core/semicore orbitals 5s, 5p, 5d, 6s, and 6p as well as configurations with electrons in the 6f−9f, 7d−9d, 8p−9p, and 8s−9s shells. Since the energetic position of the bare inner core relative to valence states is not expected to be notably relevant for chemical processes, the fit was restricted to the chemically more significant energy differences between valence states; i.e., a global shift was applied to all reference energies and treated as an additional parameter to be optimized[17]

$$\sum_I (\omega_I[E_I^{PP} - E_I^{AE} + \Delta E_{shift}]^2) := \min. \qquad (1)$$

Here, E_I^{PP} and E_I^{AE} are the PP total valence energies and the AE valence energies (i.e., total energy minus energy of the bare core), respectively. The weights ω_I were chosen to be equal for all *J* levels arising from a nonrelativistic configuration and all nonrelativistic configurations were assigned to have equal weights. The global shift ΔE_{shift} allows for the usage of configurations including core/semicore holes and can improve the accuracy of the fit by 1 or 2 orders of magnitude.

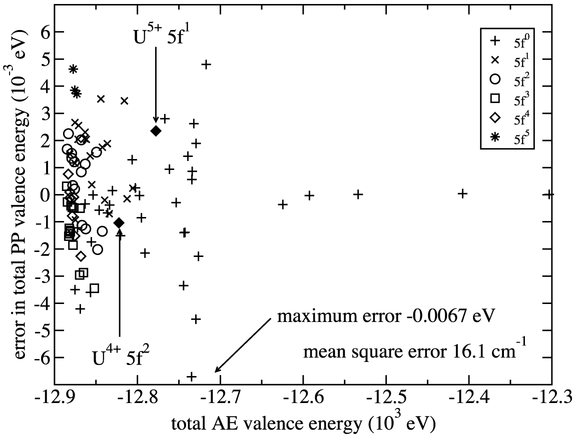

Figure 1. Errors (eV) in total valence energies of 100 nonrelativistic configurations for the MCDHF/DCB Fermi nucleus adjusted uranium small-core PP. The two configurations considered in this work are marked by filled diamonds.

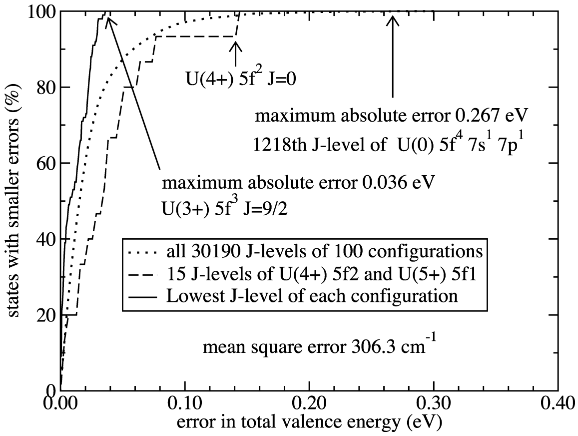

Figure 2. Percentage (%) of the *J* levels with errors in the total valence energy below the threshold (eV) indicated on the abscissa for the MCDHF/DCB Fermi nucleus adjusted uranium small-core PP. The 15 *J* levels considered in this work are marked by a dashed line.

Figures 1 and 2 summarize the accuracy of the fit for the 100 configurations and 30190 *J* levels, respectively. The mean square error for the total valence energies of configurations was 16 cm^{-1}, and for the 30190 *J* levels 306 cm^{-1}. The data for the U^{5+} $5f^1$ and U^{4+} $5f^2$ configurations considered here are marked specifically in these plots. It is obvious that the PP fit was not more accurate for these two cases than for the other configurations used in the reference data. Thus, we assume that the quality of the results obtained here is representative of what could be obtained for other configurations, provided such large-scale calculations as presented here for U^{5+} $5f^1$ and U^{4+} $5f^2$ become generally feasible. The g-part of the PP finally was adjusted to the eight energetically lowest U^{31+} [Kr] $4d^{10}4f^{14}ng^1$ ($n = 5-12$) configurations.

The basis set optimization comprised four steps.[20] First, (14s11p8d8f) primitive Gaussians were HF energy-optimized[34] for the U [Rn] $5f^47s^2$ ^5I state. Second, two diffuse d and p functions were HF energy-optimized[34] for U [Rn] $5f^36d^17s^2$ ^5L and U [Rn] $5f^37s^27p^1$ ^5K, respectively. Third, the atomic natural orbital (ANO) contraction coefficients for the resulting (14s13p10d8f)/[6s6p5d4f] set were obtained from averaged density matrices for the lowest LS states of U [Rn] $5f^36d^17s^2$ and U [Rn] $5f^47s^2$.[35] In the case of U [Rn]

$5f^47s^2$ it was possible to perform a complete active space multiconfiguration self-consistent field (CASSCF) calculation with a subsequent MRCI calculation (5s, 5p, and 5d shells were frozen), whereas U [Rn] $5f^36d^17s^2$ could only be treated at the CASSCF level. Finally, six g exponents were chosen identically to the six largest f exponents and a generalized ANO contraction was derived for U [Rn] $5f^47s^2$ yielding the final (14s13p10d8f6g)/[6s6p5d4f3g] set of roughly polarized valence quadruple-ζ (pVQZ) quality. The PP and basis set parameters are compiled in the electronic Supporting Information of this publication.

U^{5+} has only one 5f electron with a SO-free ^2F ground state. Since at the SO-free level of the calculation only one reference state is present, dynamic correlation cannot be included via an effective Hamiltonian dressing procedure. The orbital basis was obtained from a CASSCF calculation using the MCDHF/DCB PP and the corresponding (14s13p10d8f6g)/[6s6p5d4f3g] basis set on ^2F in MOLCAS[36] and the SO splitting between the $^2F_{5/2}$ ground and the $^2F_{7/2}$ excited state was calculated at the MCDHF/DCB PP SO-CI level using the EPCISO program.[24] In order to determine the best choice of the SO-CI configuration space, five different calculations were performed: Diagonalizing the reference only (no single excitations, No S), adding single excitations from the 5f orbitals (S-f), adding single excitations from the 5d and 5f orbitals (S-df), adding single excitations from the 6p and 5f orbitals (S-pf), and including all single excitations from the 6p, 5d, and 5f orbitals (S-pdf). Note that for an atom single excitations from the s shells do not contribute.

All possible LS states of U^{4+} ($5f^2$ subconfiguration) were calculated at the state-averaged CASSCF/MRCI level[35] with and without DaC using the MCDHF/DCB PP and the corresponding (14s13p10d8f6g)/[6s6p5d4f3g] basis set (^1G, ^1D, ^1I, ^1S, ^3H, ^3F, ^3P). As comparison the same calculations were also performed using the old 5f-in-valence WB PP[8] and its corresponding (14s13p10d8f6g)/[6s6p5d4f3g] basis set.[9] Two different kinds of frozen-orbital spaces were used; i.e., the 5s, 5p, and 5d orbitals were either frozen or correlated.

In the SO-CI calculation[24] of U^{4+} all 91 determinants generated by distributing two electrons in the 5f shell were included. The orbital basis was obtained from a MCDHF/DCB PP CASSCF calculation[36] on the triplet states of U^{4+}, where the orbitals were simultaneously optimized for all states. The (14s13p10d8f6g)/[6s6p5d4f3g] basis set corresponding to the PP was used and as configuration space the reference including all single excitations from the 6p, 5d, and 5f orbitals (S-pdf) was chosen, because it gave the best results for the U^{5+} SO splitting (cf. section 3.1). The lacking dynamic correlation was included via a dressed effective Hamiltonian approach defined by the projection of the correlated SO free PP CASSCF/MRCI energies onto the SO-CI space.[24,25] SO integrals were calculated with the semilocal relativistic effective SO operators corresponding to the MCDHF/DCB PP. As comparison analogous calculations were carried out using the old WB PP[8] and its corresponding effective SO operator designed for variational calculations[9] and (14s13p10d8f6g)/[6s6p5d4f3g] basis set.[9]

In addition to the SO-CI calculations described above IH-FSCC PP calculations using the approach of Kaldor and coworkers at the AE DHF/DCB level[6,31−33] were performed. The basis set ranged from the (14s13p10d8f6g)/[6s6p5d4f3g] standard basis set to subsets of a (16s15p12d10f8g7h7i) uncontracted set obtained from the former primitive set by adding diffuse and higher angular momentum functions. The addition of further s to i functions to this set changes the fine-structure splittings of U^{4+} and U^{5+} by less than 1 cm^{-1}. All explicitly treated electrons were correlated and excitations in all virtual orbitals were allowed. The primary model space consisted of the 5f, 6d, and 7s orbitals, whereas the intermediate model space comprised the 6−8f, 7−9d, 8−10s, 7−10p, 5−6 g orbitals; i.e., all orbitals with negative energy for the standard contracted basis set in the U^{6+} reference system were included in the model spaces. Although larger intermediate spaces were not feasible on our current hardware, we note that we obtain almost identical results for an intermediate space reduced by one orbital for s to g symmetry; i.e., the U^{4+} and U^{5+} fine-structure splittings show mean average deviations of 10 and 1 cm^{-1}, respectively. Thus, we are confident that the results presented here would not change significantly upon further increasing the intermediate space.

TABLE 1: SO Splittings ΔE(SO) (in cm^{-1}) of the ^2F Ground State of U^{5+} from SO-CI Calculations Using the MCDHF/DCB PP and the AE/DKH+AMFI Methods[23] as well as MCDHF/DCB PP IH-FSCC Calculations in Comparison to Experimental Data and AE DCB XIH-FSCC Results[a]

method[b]	ΔE(SO)	Δ(AE/PP)	Δ(exp)
exp.	7609		
DCB XIH-FSCC	7598		−11
DCB PP IH-FSCC spdfghi	7611	13	2
DCB PP IH-FSCC std.	7609		0
DCB PP No S	7828		219
AE/DKH No S	8022	194	413
DCB PP S-f	7868		259
AE/DKH S-f	8048	180	439
DCB PP S-pf	8407		798
AE/DKH S-pf	8596	189	987
DCB PP S-df	7213		−396
AE/DKH S-df	7318	105	−291
DCB PP S-pdf	7792		183
AE/DKH S-pdf	7906	114	297

[a] Δ(exp): deviations of the theoretical values from the experimental result.[26] Δ(AE/PP): deviations between the AE DCB XIH-FSCC[6] or AE/DKH results (upper line) and MCDHF/DCB PP results (lower line). Basis sets: PP std., (14s13p10d8f6g)/[6s6p5d4f3g]; spdfghi, (16s15p12d10f8g7h7i); AE/DKH (26s23p17d13f5g)/[10s9p7d5f3g]; AE DCB FSCC (37s32p24d21f12g10h9i). [b] Different definitions of the configuration space: Diagonalization of the reference only (No S), adding single excitations from the 5f orbitals (S-f), adding single excitations from the 5d and 5f orbitals (S-df), adding single excitations from the 6p, and 5f orbitals (S-pf), and including all single excitations from the 6p, 5d, and 5f orbitals (S-pdf).

3. Results and Discussion

The results for the fine structure of the U^{5+} and U^{4+} low-energy spectra from SO-CI and IH-FSCC calculations using the new MCDHF/DCB PP for uranium will be compared to computational[6,23,29,30] and experimental[26−28] data from the literature in order to demonstrate its accuracy.

3.1. U^{5+} SO Splitting. The SO splittings from SO-CI calculations with different definitions of the configuration space and IH-FSCC calculations with different basis sets using the new PP are listed in Table 1. In accordance with Hund's rules the ground state of U^{5+} is $^2F_{5/2}$. The experimental excitation energy for the $^2F_{5/2}$ to $^2F_{7/2}$ excitation or the experimental SO splitting amounts to 7609 cm^{-1}.[26] The up to now best theoretical value is 7598 cm^{-1} and deviates only by −11 cm^{-1} from the experiment. It was calculated by Infante et al.[6] using an AE DCB extrapolated IH-FSCC (XIH-FSCC) method.[37]

AE/DKH SO-CI calculations by Danilo et al.[23] using the AMFI (atomic mean-field integral) code[38] implemented in MOLCAS[36] to determine the SO integrals are also available

TABLE 2: Energy Levels with Respect to the Lowest Energy Level ^{3}H (in cm^{-1}) of U^{4+} with 5f^2 Valence Subconfiguration Computed at the SO-Free Level Using the MCDHF/DCB PP in MRCI Calculations with and without DaC and Two Different Frozen-Orbital Spaces, i.e., 5s, 5p, and 5d either (1) Frozen or (2) Correlated[a]

	MRCI			MRCI+DaC					
	(1)	(2)		(1)			(2)		
state	DCB[b]	DCB[b]	AE[c]	DCB[b]	WB[d]	AE	DCB[b]	WB[d]	AE[c]
^{3}H	0	0	0	0	0	0	0	0	0
^{3}F	3319	3488	3441	3050	3149	2887	3078	3151	3040
^{1}G	4971	5407	5173	4828	4970	4728	5227	5372	4994
^{1}D	12296	12727	12260	11355	11693	10806	11312	11611	11260
^{3}P	16204	16480	16325	14941	15341	14256	14588	14946	14495
^{1}I	17550	17013	16713	16953	17440	16296	15959	16380	15762
^{1}S	38458	40320	39822	36346	37430	35383	37240	38297	36780
m.a.d.		283		520	944		179	571	

[a] As comparison WB PP MRCI+DaC as well as AE/DKH MRCI(+DaC) results[23] and m.a.d. between the AE/DKH and the PP data are given. Basis sets: PP (14s13p10d8f6g)/[6s6p5d4f3g]; AE (26s23p17d13f5g)/[10s9p7d5f3g]. [b] MCDHF/DCB PP calculation. [c] 1s-5p orbitals were kept frozen. [d] WB PP calculation.

for comparison. Analogous to these SO-CI calculations we used five different configuration spaces in order to find out the best choice, i.e., no single excitations (No S), single excitations from 5f (S-f), single excitations from 6p and 5f (S-pf), single excitations from 5d and 5f (S-df), and single excitations from 6p, 5d, and 5f (S-pdf). For all configuration spaces the PP results are in a range of 105−194 cm^{-1} smaller than the AE/DKH results. However, these deviations are not only due to the PP approach but also connected with the different basis sets (AE (26s23p17d13f5g)/[10s9p7d5f3g], PP (14s13p10d8f6g)/[6s6p5d4f3g]) and relativistic treatments (AE DKH, PP DCB). Although both basis sets are of pVQZ quality, the AE set is based on CASPT2 (complete active space second-order perturbation theory) ANOs and the PP set on CASSCF/MRCI ANOs. At the AE MCDHF level, using a Fermi nucleus, the results for the DC and DCB Hamiltonians are 7394 and 7083 cm^{-1}, respectively. The energy difference of 311 cm^{-1} explains in part why also at the correlated level the PP results (modeling DCB) are lower than the DKH results (modeling DC). However, one also has to take into account that in the PP fit the total valence energy of $^2F_{5/2}$ is too low by 23 cm^{-1}, whereas the one of $^2F_{7/2}$ is too high by 50 cm^{-1}, resulting in an overestimation of the splitting by 73 cm^{-1} at this level of theory. The sum of these counteracting contributions suggests that the PP DCB splitting has to be by about 200 cm^{-1} lower than the AE DKH value.

In accordance with the AE/DKH calculations[23] we got the smallest errors with respect to the experimental value either using no single excitations or including all single excitations from the doubly occupied orbitals in the near valence region, i.e., from 6p, 5d, and 5f (error: No S 219, S-pdf 183 cm^{-1} (2.4%)). Due to the implicit inclusion of the Breit interaction the PP results deviate even slightly less from the experimental value than the AE/DKH results (error: S-pdf 297 cm^{-1} (3.9%)). On the basis of these findings the S-pdf configuration space was used to calculate the U^{4+} fine-structure spectrum.

The best PP results were obtained with the IH-FSCC approach of Kaldor and co-workers,[32,33] i.e., splittings of 7609 cm^{-1} for the standard (14s13p10d8f6g)/[6s6p5d4f3g] basis set and 7611 cm^{-1} for a (16s15p12d10f8g7h7i) uncontracted basis set. These excellent results are certainly somehow fortuitous, since the mean square error of the PP fit to the AE DHF/DCB reference data is 306 cm^{-1} for 30190 *J* levels arising from 100 configurations of U to U^{7+}. On the other hand the number is quite stable with respect to changes of the basis set; i.e., one obtains 7575 and 7597 cm^{-1} for the uncontracted subsets of (16s15p12d10f8g7h7i) containing only up to g and h functions, respectively.

Before we turn to the discussion of U^{4+}, we want to comment on results obtained with the older WB PP.[8] For this PP two valence SO terms acting on 5f, 6d, 7p, and higher orbitals of these angular momenta were published,[9] i.e., one for use in first-order perturbation theory, the other one for use in valence variational or large-scale valence SO-CI calculations. At the variational and perturbative finite difference level[21] these operators lead for U^{5+} to SO splittings of 6379 and 6590 cm^{-1}, respectively. Using the variational operator the valence SO-CI (S-f) leads to a value of 6374 cm^{-1}, demonstrating that the orbital relaxation under the SO term is very well recovered by the single excitations. However, compared to the experimental value of 7609 cm^{-1} these SO splittings are by about 15% too small. The reasons for this are missing correlation contributions in the SO-CI (S-f) and probably frozen-core errors. Note that these SO terms, as the WB PP itself, were adjusted to U and U$^+$ to reproduce MCDHF splittings arising from the 5f, 6d, and 7p shells and only configurations with a 5f occupation of two to four were considered. For U^{5+} a SO splitting of 7083 cm^{-1} is obtained at the AE MCDHF/DCB Fermi nucleus level, i.e., a value smaller by 526 cm^{-1} than the experimental value results from neglecting electron correlation effects. In contrast to this the new MCDHF/DCB PP tested here was adjusted also to U^{5+} and allows a variational or large-scale SO-CI treatment for all orbitals treated explicitly, thus explaining the better results.

3.2. U^{4+} Fine-Structure Spectrum.

In this section first the SO-free correlated energies using the new MCDHF/DCB PP for U^{4+} with 5f^2 valence subconfiguration will be discussed in comparison to WB PP and AE/DKH[23] calculations (cf. Table 2). Next the SO effect will be taken into account and the results will be compared to WB PP calculations as well as to experimental[27,28] and computational[6,23,29,30] data from the literature (cf. Tables 3 and 4).

3.2.1. SO-Free Calculations.

At the SO-free level the ground state of U^{4+} with 5f^2 valence subconfiguration is ^{3}H as expected by Hund's rules. The MCDHF/DCB PP MRCI method with and without size-extensivity correction (DaC) was used in connection with different frozen-orbital spaces, i.e., 5s, 5p, and 5d were either frozen or correlated. First we will discuss the effect of the DaC and then that of the frozen-orbital space each with respect to the AE/DKH calculations.[23] Finally, we will compare the new MCDHF/DCB PP to the old WB PP.

The MRCI method always yields higher energy levels than the MRCI+DaC method. Especially the ^{1}S state is influenced by the size-extensivity correction; i.e., it is lowered by 2112 and 3080 cm^{-1} for 5s, 5p, and 5d frozen and correlated,

TABLE 3: Energy Levels with Respect to the Lowest Energy Level $^3H_4$ (in cm^{-1}) and m.a.e. with Respect to Experimental[27,28] Data (cf. Table 4) of U^{4+} with $5f^2$ Valence Subconfiguration[a]

		MRCI		MRCI+DaC					
		(1)	(2)	(1)			(2)		
J	weight of LS state[c]	DCB[b]	DCB[b]	DCB[b]	WB[d]	AE	DCB[b]	WB[d]	AE[e]
4	85% ^{3}H+9% ^{1}G	0	0	0	0	0	0	0	0
2	83% ^{3}F+11% ^{1}D	4919	5066	4605	4508	4404	4585	4470	4559
5	95% ^{3}H	6150	6110	6165	5087	6406	6128	5055	6379
3	95% ^{3}F	9544	9664	9305	8290	9371	9295	8261	9490
4	47% ^{3}F+40% ^{1}G	9790	10011	9624	8665	9729	9765	8798	9883
6	91% ^{3}H	11685	11628	11681	9797	12054	11609	9742	12005
2	54% ^{1}D+31% ^{3}P +10% ^{3}F	*18710*	*19011*	*17803*	*16983*	*17434*	*17640*	*16795*	*17740*
4	47% ^{3}F+46% ^{1}G	*17029*	*17262*	*16851*	*14768*	*17192*	*17006*	*14932*	*17358*
0	89% ^{3}P	20104	20409	18873	18657	18157	18573	18298	18431
1	95% ^{3}P	22695	22916	21513	20677	21009	21142	20263	21210
6	91% ^{1}I	25265	24734	24733	23749	24395	23792	22716	23882
2	63% ^{3}P+30% ^{1}D	27250	27512	26172	24392	25969	25899	24066	26234
0	89% ^{1}S	47970	49613	46031	45066	45367	46772	45820	46602
	m.a.e.	1689	1929	1043	1046	887	948	952	1078

[a] The SO-free correlated energies obtained at the MRCI(+DaC) level using both the MCDHF/DCB PP and the WB PP with different frozen-orbital spaces, i.e., 5s, 5p, and 5d either (1) frozen or (2) correlated, were used to dress the SO-CI matrix. As comparison AE/DKH+AMFI MRCI+DaC data[23] are given. Changes in the ordering of states are listed in italics. Basis sets: PP (14s13p10d8f6g)/[6s6p5d4f3g]; AE (26s23p17d13f5g)/[10s9p7d5f3g]. [b] MCDHF/DCB PP calculation. [c] Only weights from the MCDHF/DCB PP MRCI+DaC calculation with no frozen orbitals larger than 8% are given. [d] WB PP calculation. [e] 1s−5p orbitals were kept frozen.

TABLE 4: Comparison of the Best MCDHF/DCB PP Results to Other Computational[6,23,30] and Experimental[27,28] Data for the Energy Levels with Respect to the Lowest Energy Level $^3H_4$ of U^{4+} with $5f^2$ Valence Subconfiguration[a] (in cm^{-1})

J	DCB PP[b] SO-CI	DCB PP[c] SO-CI	DCB PP[d] IH-FSCC	DCB PP[e] IH-FSCC	AE DKH[f] SO-CI	AE DCB[g] MCDF+CI	AE DCB[h] XIH-FSCC	exp.
4	0	0	0	0	0	0	0	0
2	4585	4406	3959	4233	4501	3844	4202	4161
5	6128	6162	5902	5890	6392	6012	6070	6137
3	9295	9191	8612	8825	9455	8624	8974	8984
4	9765	9583	9196	9264	9819	9278	9404	9434
6	11609	11608	11178	11144	12010	11116	11420	11514
2	*17640*	*17195*	15998	*16601*	*17531*	15816	16554	16465
4	*17006*	*16807*	16181	*16221*	*17289*	15853	16630	16656
0	18573	18532	17025	17960	18170	16199	17837	17128
1	21142	21112	19529	20420	20960	18942	20441	19819
6	23792	23065	22594	22441	23744	22131	22534	22276
2	25899	25659	24042	24799	25998	23379	24991	24653
0	46772	46583	43783	45329	46189	43847	45611	43614
m.a.e.	948	755	318	420	935	522	357	0
m.a.d.	628	436	567	162	616	802	0	357

[a] Mean absolute errors (m.a.e.) with respect to experimental data and mean absolute deviations (m.a.d.) with respect to AE DCB XIH-FSCC data are given; changes in the ordering of states are marked in italics. [b] MCDHF/DCB PP, MRCI+DaC + SO-CI, no frozen orbitals, (14s13p10d8f6g)/[6s6p5d4f3g] basis set. [c] MCDHF/DCB PP, IH-FSCC + SO-CI, no frozen orbitals, (14s13p10d8f6g)/[6s6p5d4f3g] basis set, LS state energies from PP IH-FSCC using a (16s15p12d10f8g7h7i) basis set. [d] MCDHF/DCB PP, IH-FSCC, no frozen orbitals, (14s13p10d8f6g)/[6s6p5d4f3g] basis set. [e] MCDHF/DCB PP, IH-FSCC, no frozen orbitals, (16s15p12d10f8g7h7i) basis set. [f] AE DKH MRCI+DaC + AMFI SO-CI, 1s-5p frozen, 5f-6d active, (26s23p17d13f5g)/[10s9p7d5f3g] basis set.[23] [g] AE DCB MCDF-CI+DaC, (1s1p2d3f3g2h1i) spinors to describe the virtual space.[30] [h] AE DCB XIH-FSCC, (37s32p24d21f12g10h9i) basis set.[6]

respectively. For the other states the changes are smaller than 1900 cm^{-1}. Compared to the AE/DKH data the calculation at the MRCI+DaC level shows better agreement; i.e., if 5s, 5p, and 5d are also correlated, the mean absolute errors (m.a.e.) for all energy levels amount to 283 and 179 cm^{-1} for MRCI and MRCI+DaC, respectively. We used the same definition of the m.a.e. as Danilo et al.[23] and Infante et al.;[6] i.e., the sum of the absolute deviations between the PP and AE/DKH energies was divided by the number, namely 6, of excited levels. However, here one should rather use the term mean absolute deviation (m.a.d.) instead of m.a.e., since in contrast to the new PP the AE/DKH calculations do not include the Breit interaction and therefore the differences do not result only from the PP approach.

The different frozen-orbital spaces influence the energy levels by at most 1862 cm^{-1}. At the MRCI level the ^{1}S state is shifted the most (−1862 cm^{-1}), while at the MRCI+DaC level the ^{1}I as well as the ^{1}S states are displaced by similar amounts, but in different directions; i.e., the ^{1}I state is lowered by 994 cm^{-1} and the ^{1}S state is increased by 894 cm^{-1}, respectively. At the MRCI+DaC level the PP results with 5s, 5p, and 5d correlated agree much better with the AE/DKH results (m.a.d. 179 cm^{-1}) than with 5s, 5p, and 5d frozen (m.a.d. 520 cm^{-1}). However, while in the latter case the AE and PP correlation spaces are exactly the same, they differ by frozen 5s and 5p shells at the AE level in the former case. The PP results obtained with 5s and 5p frozen exhibit a m.a.d. of 514 cm^{-1} to the corresponding AE values. For the PP SO-CI calculations reported below only the term energies with either 5s, 5p, and 5d frozen or correlated were considered.

If the old WB PP is used, the energy levels are always higher than those using the new MCDHF/DCB PP, whereby the increase grows from the ^{3}F to ^{1}S state, where it reaches more than 1000 cm^{-1}. Since the new PP already overestimates the AE/DKH energy levels, the m.a.d. are clearly larger using the old WB instead of the new MCDHF/DCB PP, i.e., the m.a.d. at the MRCI+DaC level using the new/old PP amount to 520/944 and 179/571 cm^{-1} for 5s, 5p, 5d frozen and correlated, respectively.

3.2.2. SO Calculations. Table 3 shows the results for U^{4+} obtained at the SO-CI level by dressing the effective Hamiltonian matrix with MRCI(+DaC) correlated energies for the LS states calculated using both the new MCDHF/DCB and old WB PP and two different frozen-orbital spaces. For comparison results of corresponding AE/DKH MRCI+DaC dressed effective Hamiltonian SO-CI calculations by Danilo et al.[23] are listed. The values included here are not the best results from this work (cf. Table 4), but merely those for which the correlation space fits best to the listed PP calculations. The second column of Table 3 presents information on the main SO-free states contributing to each SO state. The weights were obtained from a MCDHF/DCB PP calculation with a MRCI + DaC (no frozen orbitals) dressing of the effective spin−orbit Hamiltonian. Additionally, m.a.e. with respect to the experimental data[27,28] (cf. Table 4) are given, which were calculated analogous to Danilo et al.[23] and Infante et al.;[6] i.e., the sum of the absolute deviations between the calculated and experimental energy levels was divided by the number, namely, 12, of excited levels. Analogous to the SO-free calculations we will first discuss the effect of the size-extensivity correction (DaC) and then the difference between the two frozen-orbital spaces. Next we will compare the results using the new MCDHF/DCB PP to that using the old WB PP as well as to AE/DKH calculations.[23] Finally, we will give a comparison with other theoretical works[6,29,30] (cf. Table 4).

As for the SO-free calculations the MRCI method yields higher energy levels than the MRCI+DaC method except for the ^{3}H$_5$ state, which is slightly increased by 15 and 18 cm^{-1} for 5s, 5p, and 5d frozen and correlated, respectively, if the DaC is applied. Since the experimental energy levels are already overestimated by the MRCI+DaC results, the neglect of the size-extensivity correction leads to clearly increased deviations, i.e., the m.a.e. amount to 1689/1043 and 1929/948 cm^{-1} for MRCI/MRCI+DaC calculations with 5s, 5p, and 5d frozen and correlated, respectively. Except for the ^{3}H$_5$ state all energy levels come closer to experiment and the largest improvement by 1939 (5s5p5d frozen) and 2841 cm^{-1} (5s5p5d correlated) is observed for the ^{1}S$_0$ state. Thus, the size-extensivity correction gives a clear improvement of the results. Therefore, the following discussions will be restricted to the MRCI+DaC method.

At this level the correlation of the 5s, 5p, and 5d orbitals leads to an improvement of the results; i.e., the m.a.e. decreases from 1043 to 948 cm^{-1}. This is due to the fact that the energy levels are lowered, if no orbitals are frozen, except for the two (^{3}F, ^{1}G)$_4$ states and the ^{1}S$_0$ state, where the energy levels are increased by 141, 155, and 741 cm^{-1}, respectively. The largest improvement due to the increased correlation space is obtained for the ^{1}I$_6$ state and amounts to 941 cm^{-1}.

Compared to the old WB PP the new MCDHF/DCB PP seems not to improve the results; i.e., the m.a.e. differ by at most 4 cm^{-1}. However, this is most likely due to an error cancellation at the WB PP level, because the underlying relativistic approach is more accurate for the new PP. The WB PP energy levels are always lower than those of the MCDHF/DCB PP and the maximum deviations are found for the higher (^{3}F, ^{1}G)$_4$ state and amount to 2083 and 2074 cm^{-1} for 5s, 5p, and 5d frozen and correlated, respectively. While the new PP always overestimates the experimental energy levels, they are both over- and underestimated by the old PP. Thus, the new PP seems at least to be more systematic in its deviations.

Analogous to the MCDHF/DCB PP the AE/DKH calculations always overestimate the experimental energy levels. If the 5s, 5p, and 5d orbitals are frozen, the PP energy levels are mainly larger than those of the AE/DKH calculations, and thus the m.a.e. is by 156 cm^{-1} larger than that of the AE/DKH values. If 5s, 5p, and 5d are correlated, the PP energy levels are mainly lower than those of the AE/DKH calculations, and thus the m.a.e. of 948 cm^{-1} (5.1%) is by 130 cm^{-1} lower than that of the AE/DKH values, i.e., m.a.e. 1078 cm^{-1} (6.3%). However, the better agreement with the experimental data for 5s, 5p, and 5d correlated is probably due to the fact that in the AE/DKH calculation the 5s and 5p orbitals were kept frozen (cf. section 3.2.1). For both PP and AE/DKH calculations the largest deviations occur for the ^{1}S$_0$ and ^{1}I$_6$ states, whereby for the smaller correlation space the ^{1}I$_6$ and for the larger one the ^{1}S$_0$ state shows the larger deviation (5s5p5d frozen: PP: ^{1}I$_6$ 2457, ^{1}S$_0$ 2417; AE/DKH: ^{1}I$_6$ 2119, ^{1}S$_0$ 1753; 5s5p5d correlated: PP: ^{1}S$_0$ 3158, ^{1}I$_6$ 1516; AE/DKH: ^{1}S$_0$ 2988, ^{1}I$_6$ 1606 cm^{-1}).

Table 4 summarizes our best results and compares them to selected computational ab initio data from the literature.[6,23,30] As mentioned above the m.a.e. with respect to the experiment of both PPs are almost the same; i.e.. they amount to 948 (5.1%) and 952 cm^{-1} (7.2%) for the new and old PP, respectively. Thus, only the best results for the new PP from Table 3 are repeated for convenience.

The best calculations so far available for the fine structure of the U^{4+} spectrum are the AE four-component calculations using the DCB Hamiltonian at the multiconfiguration Dirac−Fock configuration interaction with Davidson correction (MCDF-CI+DaC) level[30] as well as at the XIH-FSCC level.[6] Both calculations yield the experimental ordering of the energy levels and show m.a.e. clearly below 1000 cm^{-1}, i.e., the m.a.e. amount to 522 (3.6%) and 357 cm^{-1} (1.5%) for the MCDF-CI+DaC and XIH-FSCC calculations, respectively. Therefore, these calculations, especially FSCC, are useful as benchmark data, because they indicate the highest currently accessible accuracy for ab initio approaches in a theoretical spectrum for U^{4+}.

Even if the discrepancies between the AE four-component values and our PP SO-CI results are quite large, one should keep in mind the limitations of the AE four-component methods; i.e., the current implementation of the MCDF-CI can only be applied to atoms and the FSCC calculations to systems with at most two holes and/or electrons outside the reference closed-shell system.[23] The scope of the PP as well as the dressed effective Hamiltonian SO-CI starting from states obtained by correlated calculations within the Russell−Saunders scheme is much larger and both achieve a rather good agreement with the experimental values at a relatively low computational cost despite the strong SO coupling.

In order to separate the errors originating from the PP valence-only model Hamiltonian from those due to deficiencies of the one- and many-particle basis sets, we also applied the atomic DHF and FSCC suite of programs by Kaldor, Ishikawa, and co-workers.[32,33] The IH-FSCC results for the MCDHF/DCB PP are in quite satisfactory agreement with experimental data. Using the standard (14s13p10d8f6g)/[6s6p5d4f3g] basis set a m.a.e. (m.r.e.) with respect to experimental data of only 318 cm^{-1} (2.5%) is obtained, whereas the m.a.d. from the AE DCB XIH-FSCC results of Infante et al.[6] is 567 cm^{-1}. The corresponding results for the (16s15p12d10f8g7h7i) basis set are 420 (2.3%)

and 162 cm^{-1}, respectively. Using subsets of the uncontracted set containing up to g and h functions, m.a.d. values with respect to the AE results of Infante of 432 and 204 cm^{-1}, respectively, are obtained.

Electron correlation effects are especially large for the $^1S_0$ state, which is calculated to be 673, 1430, and 1715 cm^{-1} above the experimental value of 43614 cm^{-1} for subsets of the uncontracted set containing up to g, h, and i functions, respectively. Although the errors with respect to experiment increase upon improving the correlation treatment, we note that our result for the largest basis set deviates by only 285 cm^{-1} from the AE DCB XIH-FSCC value of 45611 cm^{-1}. A basis set extrapolation with respect to $1/l^3$, l being the highest angular quantum number present in the basis set, yields a value 2172 cm^{-1} above the experimental value. If we take into account that in the PP fit the $^1S_0$ state already is too high by 1144 cm^{-1} (cf. Figure 2), our corrected estimate would accordingly be a term energy of 44642 cm^{-1}; i.e., the overestimation arising from the FSCC treatment could amount to about 1000 cm^{-1}. On the other hand it is fair to note that the $^1S_0$ state was originally not observed by Wyart et al. and its term energy has been semiempirically estimated to be 45812 cm^{-1}.[27] A refined estimate by Goldschmidt placed it at 45154 cm^{-1}.[39] Finally, Van Deurzen et al. applied in their model Hamiltonian a γ parameter taken from the fitting of the spectra of *trivalent* actinides in crystals and estimated a value of 43480 cm^{-1}.[28] On the basis of this value three lines in the emission spectrum were interpreted as transitions from $^3D_1$, $^3P_1$, and $^1P_1$ of $5f^16d^1$ to $^1S_0$ of $5f^2$, and applying the term energies of $5f^16d^1$ by Wyart et al.,[27] the term energy of $^1S_0$ has been determined to be 43614 cm^{-1}.[28] More rigorous ab initio calculations than the ones reported here and in the literature so far are needed to clarify the situation.

Despite the smooth convergence of the PP results toward the AE results, the ordering of the $(^3F, ^1G)_4$ and $(^1D, ^3P)_2$ levels near 16500 cm^{-1} is not reproduced correctly at the PP level with uncontracted basis sets, in contrast to the AE results. A notable exception is the standard contracted basis set, where the correct ordering of the states and the smallest error for the $^1S_0$ state is obtained. At the AE finite difference MCDHF/DCB Fermi nucleus level $(^1D, ^3P)_2$ is 5263 cm^{-1} above $(^3F, ^1G)_4$,[21] whereas experimentally it is 191 cm^{-1} below. Thus, the calculations have to recover accurately quite large differential correlation contributions. Otherwise the contributions to the fine structure are quite accurately folded into the effective one-electron spin−orbit term, which yields stable results already for comparatively small basis sets.

Deviations of a few hundred wavenumbers from experimental and highly accurate AE data have to be expected due to the accuracy of the PP adjustment. Thus it is clear that an even better agreement with experimental data than that obtained in the rigorous AE calculations is to a certain extent fortuitous. The question why the two-step SO-CI calculations exhibit larger errors was investigated by applying energies from IH-FSCC calculations using the scalar-relativistic part of the MCDHF/DCB PP and the (16s15p12d10f8g7h7i) basis set as diagonal elements in the SO-CI matrix, which was built using the standard basis set. The SO-CI and FSCC term energies up to 15000, between 15000 and 30000, and above 30000 cm^{-1} agree with a m.a.d. of 420, 1167, and 2800 cm^{-1}, respectively, when the standard basis set is applied in the FSCC. Corresponding m.a.d. of 319, 655, and 1254 cm^{-1} are obtained with respect to FSCC results calculated with the (16s15p12d10f8g7h7i) basis set. The m.a.e. (m.r.e.) for all levels listed in Table 4 with respect to experimental data is reduced from 948 (5.1%) to 755 cm^{-1} (3.8%); i.e., about 40% of the remaining error comes from the energies of the LS states whereas about 60% might be caused by insufficient orbital relaxation under the SO term.

TABLE 5: Ionization Potentials (in cm^{-1}) U^{4+} and U^{5+} from MCDHF/DCB PP IH-FSCC Calculations in Comparison to Corresponding AE DHF/DCB XIH-FSCC Results

method	IP$_5$	ΔIP$_5$	IP$_6$	ΔIP$_6$
DCB XIH-FSCC[a]	381074	0	508183	0
DCB PP std.[b]	381617	543	507904	−279
DCB PP spdf[c]	367431	−13643	491960	−16223
DCB PP spdfg[c]	378377	−2697	504299	−3884
DCB PP spdfgh[c]	381118	44	507170	−1013
DCB PP spdfghi[c]	382297	1223	508451	268
DCB PP ext.[c]	383960		510195	

[a] AE DCB XIH-FSCC (37s32p24d21f12g10h9i).[6] [b] (14s13p10d8f6g)/[6s6p5d4f3g] standard PP basis set. [c] spdf... spdfghi denotes a subset of a (16s15p12d10f8g7h7i) basis set; ext. denotes extrapolated values based on results obtained with the spdfg, spdfgh, and spdfghi basis sets.

Barandiarán and Seijo[29] also performed a two-step method, where they used CASPT2 applying a WB ab initio model potential (1s−5d in core) to dress the SO-CI matrix. Their best results agree even better with the experiment than the AE four-component methods; i.e., the m.a.e. amounts to only 180 cm^{-1} (1.4%). However the reason for this very good agreement is, at least in part, due to parameter fitting; i.e., a scaling factor of 0.9 was applied to the WB SO operator and the ^3P and ^1I states were shifted downward by 1000 cm^{-1}. It is noteworthy that without these corrections the m.a.e. is much larger (1284 cm^{-1} (8.3%)), whereas the ordering of the states is entirely correct with $(^1D, ^3P)_2$ being about 327 cm^{-1} below $(^3F, ^1G)_4$ (experiment 191 cm^{-1}).

3.2.3. Ionization Potentials. The fifth and sixth ionization potentials of U are obtained as a byproduct of the IH-FSCC calculations. The corresponding results are listed in Table 5. The values obtained with the contracted standard basis set deviate by only 543 and −279 cm^{-1} from the best corresponding AE data published by Infante et al.[6] Using the uncontracted basis set and monitoring the behavior with respect to the highest angular momentum quantum number in the basis set, one finds a systematic convergence, although the deviations from the AE values tend to become somewhat larger. Extrapolating the PP results linearly for the largest three basis sets with respect to $1/l^3$, with l being the highest angular momentum quantum number present in the basis set, we obtain values of 383960 and 510195 cm^{-1} for IP$_5$ and IP$_6$, respectively. The correlation coefficients deviate from the ideal value of -1 only by 2×10^{-5} and 2×10^{-6}, respectively. The extrapolated PP values are by 0.75% and 0.40% higher than the AE results, which are most likely also not fully converged with respect to the basis set. It should be noted here that experimental reference values do not exist.

4. Conclusion

The SO-CI calculation using the new MCDHF/DCB PP for the SO splitting of U^{5+} yields good agreement with the experiment; i.e., the deviation is 183 cm^{-1} corresponding to 2.4%. Analogous to the AE/DKH+AMFI calculations we get the best results for the SO-CI configuration space, where all single excitations from the doubly occupied orbitals in the near valence region are included, i.e., from 6p, 5d, and 5f. Therefore, this configuration space was used to calculate the fine structure of the U^{4+} spectrum.

For the U^{4+} spectrum the SO-CI using the MCDHF/DCB PP with a MRCI+DaC dressing (no frozen orbitals) of the effective Hamiltonian gave the best results; i.e., the m.a.e. with respect to the experimental data amounts to 948 cm^{-1} corresponding to 5.1%. All energy levels are systematically overestimated by the new PP and the maximum deviation found for the $^1S_0$ state is 3158 cm^{-1}. Although the old WB PP yields a similar m.a.e. of 952 cm^{-1}, it is less systematic, because the energy levels are both over- and underestimated. The results of the new PP are in reasonable agreement with the AE/DKH MRCI+DaC calculations. An accuracy very similar to the one obtained in AE four-component MCDF-CI+DaC and XIH-FSCC calculations is obtained when the new PP is applied in the IH-FSCC framework; i.e., for the largest basis set a virtually exact splitting for U^{5+} and a m.a.e. of 420 cm^{-1} for U^{4+} are found. In view of applications in larger molecular systems, it is very promising that due to the folding of the relativistic effects including spin−orbit coupling into an effective one-electron Hamiltonian in the PP approach, results of this quality can already be obtained using standard contracted basis sets of valence polarized quadruple-ζ quality.

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Supporting Information Available: Listings of the pseudopotential and basis set parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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