Nodeless Valence (Pseudo)spinors

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Atomic calculations using small-core relativistic effective core potentials (RECPs) explicitly treating outer core electrons are used to define two-component nodeless valence spinors (NVSs) and nodeless valence pseudospinors (NVPSs). Errors attributable to nonlocal electron repulsion interactions that arise from large-core RECPs are shown to result from the inherent arbitrariness in the choice of match points and number of derivatives that define shape-consistent pseudospinors, as well as the positions of radial nodes that reside in the outer core regions of atoms. Self-consistent field calculations in $\omega\omega$-coupling for InH and InCl using RECPs derived from NVSs and NVPSs are reported. Increased bond distances relative to those calculated using very-large-core RECPs for In agree with those due to frozen $4d_{3/2}$ and $4d_{5/2}$ spinors and a small-core RECP. Results for AmCl+2 also reveal that the shortening in the bond length is recovered when the very-large-core RECP is derived using nodeless valence (pseudo)spinors.

1. INTRODUCTION

Relativistic effective core potentials (RECPs) derived from all-electron ab initio numerical Dirac−Fock (DF) atomic wave functions afford the ability to reduce the number of electrons that must be treated explicitly while incorporating relativistic effects that are necessary for accurate representations of molecules containing heavy elements. Since RECP-based methods rely on the principle of core/valence separability, a choice must be made regarding the number of electrons that will ultimately be treated explicitly. In the procedure developed by Lee, Ermler, and Pitzer[2] and by Christiansen, Lee, and Pitzer[3] (the LEPC method), which is the method that forms the basis for this work, there are no restrictions on this choice. That is, the limit where all subshells are defined as valence is equivalent to an all-electron treatment. However, there are constraints on the number of subshells chosen to define the core space because "core" and "valence" are not merely definitions of convenience: valence space orbitals, by definition, change as a result of chemical processes such as bonding, ionization, and excitation, whereas core orbitals do not. Consequently, defining valence orbitals as core orbitals erroneously restricts the former. Moreover, not all subshells can be placed either in the core or in the valence spaces. In many, if not most, cases certain subshells exhibit both core and valence characteristics. These subshells are termed "outer core" or "inner valence". Here the former term is preferred because these subshells are incorporated into pseudopotentials. The general subject of outer core spaces has been discussed in the context of core/valence polarization (and correlation) phenomena in terms of both frozen core[4] and pseudopotential[5] approximations. This study does not treat core/valence polarization effects. Only errors due to nonlocal effects that are revealed in the context of the frozen outer core self-consistent field (SCF) approximation, which has been

discussed previously in terms of nonrelativistic wave functions, are addressed.[6]

RECPs that include the largest possible number of electrons in the core, very-large-core RECPs (VLC RECPs), keeping in mind the above-mentioned restrictions, generally lead to bond lengths that are too short when compared to all-electron calculations. On the other hand, retaining additional subshells as valence shells, i.e., small-core RECPs (SC RECPs), generally provides sufficient flexibility, because of the greater number of explicitly treated electrons, so as to lead to good agreement with all-electron calculations. It has been reported in calculations on InCl that using a SC RECP for In led to a bond length in good agreement with all-electron Dirac−Fock results; however, the use of a VLC RECP led to an appreciably shorter bond length.[7] It is shown in this work that the above-mentioned errors are due to nonlocal electron exchange repulsion effects traceable to outer core electrons and present a modification to the LEPC procedure, making possible the derivation of corrected VLC RECPs that incorporate outer core subshells. The indium atom[8] is chosen as an example, and results are compared to those due to VLC RECPs derived using shape-consistent pseudospinors.[2,3]

2. METHOD AND CALCULATION OF RECPS

Errors due to the improper representation of nonlocal effects in the indium VLC RECP are traceable to the $5d_{3/2}$ and $5d_{5/2}$ pseudospinors used in the LEPC method, which does not define an outer core space. That is, the SC RECPs and VLC RECPs are derived in the same manner. First, an all-electron DF wave function is generated.[9] Next, nodes are removed from so-defined valence spinors by means of the shape-consistent pseudospinor procedure.[3] (Only the large components of the four-component Dirac spinors are retained in the LEPC procedure.) Finally, these nodeless two-component pseudospinors are used to derive the RECP.[2] The quality of the RECP is initially ascertained by comparing

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atomic results generated using the RECP with those due to all-electron DF calculations. This process works well for SC RECPs because the error resulting from the shape-consistent approximation is deposited overwhelmingly in the core region; viz., if nodes contained in the all-electron DF spinor occur in the core region, which is the case for SC RECPs, then the error introduced when these nodes are removed in the shape-consistent procedure remains in the core region and is unimportant. However, if the nodes occur in both the core and outer core (or inner valence) spaces, which is generally the case for VLC RECPs, then the error introduced when these nodes are removed in the shape-consistent procedure remains in the core and outer core regions. This is the error that leads to the incorrect representation of nonlocal effects as shown below. In the case of the core region, these errors are almost always small and, more importantly, can be measured against atomic all-electron DF results to make certain that they are insignificant. In the case of the outer core region, however, these errors can be appreciable, and they cannot be compared with atomic all-electron DF results to determine their magnitude because of the valence-like properties of this region. That is, to ascertain the magnitude of the errors, the results obtained from VLC RECP calculations must be validated with respect to both atomic and molecular all-electron DF results because electrons occupying this region exhibit both core (atomic) and valence (molecular) characteristics. It is clear, therefore, that to derive VLC RECPs devoid of nonlocal error the nodes in the corresponding all-electron DF spinors must be removed such that the error resulting from the shape-consistent approximation is deposited solely in the core region. Or, in the case where a spinor's nodes occur in a region corresponding to the outer core, the process by which these are removed must be less radical than that of the shape-consistent procedure (i.e., change the spinor as little as possible relative to the original Dirac−Fock spinor).

In the LEPC procedure, the RECPs are calculated by using numerical DF two-component spinors. The nodes in these spinors are removed, and the resulting pseudospinors are used to back-solve the DF equation for the RECPs. As previously stated, the resulting RECPs are accurate only when the nodes to be removed occur solely in the core region. When nodes are present in the outer core region, The RECPs generated using the LEPC procedure are inaccurate. These specific inaccuracies are remedied by making use of SC RECPs that explicitly retain outer core electrons to define new VLC RECPs. The VLC RECPs derived in this manner possess no error due to nonlocal effects emanating from the outer core. In the case of indium, the SC RECP used to derive the VLC RECP retained the $4d_{3/2}$ and $4d_{5/2}$ electrons as valence electrons. To illustrate specifically, the SC RECP of LaJohn et al.[8] is used with a valence basis set of Slater-type orbitals (STOs) to derive two-component atomic spinors (ASs), as linear combinations of STOs, viz., LCSTO-ASs, which are the 5s, $5p_{1/2}$, $5p_{3/2}$, $4d_{3/2}$, $4d_{5/2}$, $5d_{3/2}$, and $5d_{5/2}$ spinors for In. The 5s, $5p_{1/2}$, $4d_{3/2}$, and $4d_{5/2}$ spinors are contained in the ground-state In wave function. However, the $5p_{3/2}$, $5d_{3/2}$, and $5d_{5/2}$ spinors must be defined in excited-state atomic calculations, with the $5p_{3/2}$ spinor coming from a neutral In excited state and the $5d_{3/2}$, and $5d_{5/2}$ spinors from an In$^+$ state having the $5p_{1/2}$ electron ionized and one of the 5s electrons excited first to the $5d_{3/2}$ and then to the $5d_{5/2}$ subshell. (The procedure

Table 1. Basis Sets of Slater-Type Orbital Two-Component Spinors[a]

indium		hydrogen		chlorine	
nl	ζ	nl	ζ	nl	ζ
5s	7.487	1s	3.500	3s	4.080
5s	2.410	1s	1.400	3s	2.750
5s	1.391	1s	1.000	3s	1.670
		1s	0.800	3s	1.480
5p	5.574				
5p	2.018	2s	2.400	4p	6.730
5p	1.095			4p	3.120
		$2p^c$	1.300	4p	1.700
$4d^b$	13.23	$2p^c$	0.700	4p	0.960
$4d^b$	4.746				
$4d^b$	2.590			$3d^c$	2.000
$4d^b$	0.967			$3d^c$	1.000
$5d^b$	1.574				
$5d^b$	0.993				
$5d^b$	0.736				
$5d^b$	0.543				
$5d^c$	2.500				
$5d^c$	1.200				

[a] The same exponents were used for both the $l - \frac{1}{2}$ and $l + \frac{1}{2}$ spinors. [b] Basis functions used in atomic In SCF calculations. [c] Polarization functions used in InH and InCl SCF calculations.

is analogous to that employed in the LEPC method for deriving RECPs.)[8] Furthermore, to define the residual potential, which is also a part of the RECP derived via the LEPC method, $4f_{5/2}$ and $4f_{7/2}$ ASs must be generated. However, these ASs are already nodeless in the DF calculation because they are the first spinors of $l = 3$ symmetry. As a result, the calculated numerical Dirac−Fock forms[9] are used to derive the corresponding RECPs for $4f_{5/2}$ and $4f_{7/2}$ and no 4f STOs are required in the atomic basis set.

The basis set of three 5s, three 5p, four 4d, and four 5d STOs (same exponents for the $l - \frac{1}{2}$ and $l + \frac{1}{2}$ components of each subshell spinor) shown in Table 1 was used to define the two-component ASs of In. The SC RECP described the In atom as [core]$4d_{3/2}^4 4d_{5/2}^6 5s^2 5p_{1/2}$. It is noted that, in subsequent InH and InCl calculations, the VLC RECP described the In atom as [core′]$5s^2 5p_{1/2}$, where [core′] consists of the original [core] plus the $4d_{3/2}^4 4d_{5/2}^6$ electrons. Consequently, the 4d STOs were omitted from the basis set in these calculations. In other words, the 4d electrons of In are not described explicitly, but rather using the VLC RECP. Furthermore, the 5d STOs were also omitted from the basis set and replaced by the two 5d polarization functions also given in Table 1. A basis set of four 1s, one 2s, and two 2p STOs was used for H and three 3s, three 3p, and two 2d STOs for Cl (Table 1) in the subsequent InH and InCl calculations. All of the STOs were optimized in either atomic or molecular calculations in the presence of an appropriate LEPC RECP.

The 5s, $5p_{1/2}$, and $5p_{3/2}$ LCSTO-ASs are calculated as nodeless as a natural outcome of the valence-electron-plus-SC RECP atomic SCF procedure. We refer to such spinors as "nodeless valence spinors" (NVSs). However, the $5d_{3/2}$ and $5d_{5/2}$ ASs contain one node because there exists a lower-lying spinor of the same symmetry in each case. The node must be removed from each spinor. We refer to spinors in which one node has been removed from a NVS as "nodeless valence pseudospinors" (NVPSs). The node can be removed by a myriad of methods.[10] In the present approach the single

Table 2. Indium Valence Spinors and Pseudospinors

5s	5p$_{1/2}$	5p$_{3/2}$	4d$_{3/2}$	5d$_{3/2}$[a]	5d$_{3/2}$′[a]	4d$_{5/2}$	5d$_{5/2}$[a]	5d$_{5/2}$′[a]
0.0162	0.0166	0.0103	−0.0132	0.0021	0.0000	−0.0126	0.0020	0.0000
0.6952	0.5826	0.5338	0.7019	−0.1119	0.0000	0.6831	−0.1106	0.0000
0.3899	0.5309	0.5811	0.3859	−0.0202	0.0000	0.4077	−0.0263	0.0000
			0.0105	−0.1674	0.0000	0.0058	−0.1755	0.0000
			0.0000	0.2880	0.2338	0.0000	0.2903	0.2352
			0.0000	0.6861	0.5983	0.0000	0.6855	0.5967
			0.0000	0.2849	0.2469	0.0000	0.2949	0.2486
			0.0000	0.0030	0.0020	0.0000	0.0005	0.0003

[a] Based on SC RECP frozen 5s and 4d$_{3/2,5/2}$ spinors relative to the STO basis set of Table 1.

node in each spinor is eliminated by constraining the coefficients of the $n = 5$ spinor in such a way that the STOs corresponding to the $n = 4$ spinor (i.e., the 4d STOs) do not contribute. Since the latter is necessarily constrained to be frozen in its ground-state form, the coefficients of the $n = 5$ basis functions are zero by definition. Operationally, this is achieved by requiring all coefficients of $n = 5$ STOs in $n = 4$ ASs to be zero at every iteration in an atomic SCF calculation, thus allowing the $n = 5$ spinor to relax self-consistently while retaining a nodeless form. The $l = 2$ LCSTO-ASs, both prior to and following the constraint on the $n = 5$ ASs, are shown in Table 2.

This procedure removes the node in an outer core AS more accurately than the shape-consistent procedure because the form of the AS is retained as a bona fide eigenvector of the valence electron Fock matrix[2] over its entire radial range (from the atomic nucleus to infinity). This is a particularly important advantage in the present procedure since nodes are removed in the outer core region, which in the shape-consistent pseudospinor method, occurs to the left (inside) of the match point. In the shape-consistent pseudospinor approach the spinor has the form of a power series expansion from a chosen match point inward to the nucleus.

These nodeless two-component ASs (NVSs and NVPSs) shown in Table 2 are next expanded over the same quadrature as the corresponding numerical Dirac−Fock spinors.[9] Finally, a new VLC RECP, which we refer to as a nodeless valence (pseudo)spinor RECP (NV RECP), is derived in the form of a numerical operator by the identical LEPC procedure used to obtain the original SC RECP.[8] Atomic SCF calculations were also performed in which the 4d$_{3/2}$ and 4d$_{5/2}$ spinors of In were frozen at their ground-state forms while employing the SC RECP. (This is the proper calculation for direct comparison to the VLC RECP and NV RECP result.)

3. RESULTS AND DISCUSSION

Atomic Hartree−Fock calculations in the context of two-component Dirac spinors and jj-coupling[2] were carried out for the indium atom and cation using the STO basis set shown in Table 1, using the SC RECP and VLC RECP of LaJohn et al.,[8] and using the present NV RECP. The spinor energies and positions of the radial maxima are shown in Table 3, along with the corresponding calculated numerical DF value.[9]

It is especially noteworthy that all three RECPs show good agreement with the DF results, both for spinor energies and for spinor maxima. The largest discrepancies observed in Table 3 from column to column are on the order of a few millihartrees (6 for the 5s spinor) and 0.02 bohr in the spinor

Table 3. Indium Atomic Spinor Energies and Spinor Maxima

	$-\epsilon$ (hartrees)				r_{max} (bohrs)			
	DF	SC	VLC	NV	DF	SC	VLC	NV
In								
4d$_{3/2}$	1.027	1.030			0.93	0.91		
4d$_{5/2}$	0.991	0.992			0.94	0.95		
5s	0.393	0.387	0.393	0.387	2.24	2.23	2.23	2.23
5p$_{1/2}$	0.202	0.202	0.202	0.204	2.89	2.87	2.87	2.89
5p$_{3/2}$	0.192	0.192	0.192	0.193	3.00	3.01	3.01	3.01
5d$_{3/2}$	0.057	0.057	0.059	0.059				
5d$_{5/2}$	0.057	0.057	0.060	0.058				
In$^+$								
5d$_{3/2}$	0.219	0.215	0.213	0.211	4.70	4.70	4.72	4.73
5d$_{5/2}$	0.218	0.214	0.212	0.211	4.73	4.73	4.72	4.73
4f$_{5/2}$	0.127	0.126		0.126	7.80			7.80
4f$_{7/2}$	0.127	0.126		0.126	7.80			7.80

maxima. Thus, it is impossible to determine which form of RECP is more accurate on the basis of SCF calculations on the neutral or cationic atom.

The principal difference between the VLC RECP and NV RECP is traced to the form of the 5d$_{3/2}$ and 5d$_{5/2}$ pseudo (nodeless valence) spinor. The VLC RECP pseudospinors were derived using the shape-consistent spinor algorithm of Christiansen et al.[3] In this procedure the outer portion (valence portion) of the spinors are identical to the original large component of the numerical Dirac spinor. The radial portion of the pseudospinor from the so-called match point in to the nucleus (the core portion) is fitted such that five derivatives of the spinor are equivalent at the match point. Thus, the shape-consistent pseudospinor has its shape determined by a power series fit from the match point inward. The nodeless valence spinors (Table 2), on the other hand, are linear combinations of STOs that are determined by a self-consistent field procedure in the presence of the SC RECP. Particularly, those portions of the 5d$_{3/2}$ and 5d$_{5/2}$ spinors that lie in the outer core region defined by the filled 4d$_{3/2}$ and 4d$_{5/2}$ spinors (Table 3) possess shapes that correspond to SCF spinors, as opposed to fits that are required to be smooth from the match point in to the nucleus. In the case of indium, match points based on the shape-consistent pseudospinor method[3] are chosen as 1.12, 131, 1.32, 0.51, and 0.51 Å for the 5s, 5p$_{1/2}$, 5p$_{3/2}$, 4d$_{3/2}$, and 4d$_{5/2}$ ASs, respectively. By contrast values of 1.95 Å are appropriate for both the 5d$_{3/2}$ and 5d$_{5/2}$ outer spinors when the 4d$_{3/2}$ and 4d$_{5/2}$ ASs are defined as core subshells. As a result, the difference between the VLC RECP and NV RECP is traced solely to the forms of the 5s, 5p$_{1/2}$, 5p$_{3/2}$, 5d$_{3/2}$, and 5d$_{5/2}$ nodeless valence (pseudo)spinors used in the derivation of the RECP. This difference is revealed only in molecular calculations and is identified with the errors in the local approximation of the outer core subshells due to the shape-

Table 4. InH LCAS-MS SCF Results[a]

property	SC	SC(F)	VLC	NV	exptl[b]
E_{val}[c]	−57.3041	−57.3015	−2.3859	−2.3824	
$1\epsilon_{1/2}$[d]	−1.030	−1.031			
$2\epsilon_{1/2}$	−0.996	−0.995			
$3\epsilon_{1/2}$	−0.474	−0.475	−0.480	−0.473	
$4\epsilon_{1/2}$	−0.280	−0.279	−0.282	−0.279	
$1\epsilon_{3/2}$	−1.035	−1.034			
$2\epsilon_{3/2}$	−0.995	−0.987			
$1\epsilon_{5/2}$	−1.002	−0.999			
δ_{In}[e]	0.00	0.00	−0.01	−0.01	
μ[f]	−0.38	−0.40	−0.57	−0.45	
ω_e[g]	1531	1535	1529	1533	1476
$\omega_e x_e$[h]	21.3	21.7	21.9	23.7	25.6
R_e[i]	1.843	1.863	1.811	1.863	1.838

[a] Molecular self-consistent field results in the context of the indicated RECP and two-component spinor basis set (Table 1). [b] Huber, K. P., Herzberg, G. *Molecular Structure and Molecular Spectra. IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979. [c] Total valence electron energy (hartrees) at the calculated R_e. [d] Molecular spinor energies (hartrees) at the calculated R_e. [e] Mulliken net charge at the calculated R_e. [f] Dipole moment (D) at R_{exptl}. [g] Harmonic frequency (cm^{-1}). [h] Anharmonicity constant (cm^{-1}). [i] Equilibrium bond length (Å).

consistent forms chosen for the VLC RECP. In the present procedure the nonlocal effects due to the $4d_{3/2}$ and $4d_{5/2}$, which are explicitly present when the SC RECP is used, are transferred directly into the NV RECP through the $5d_{3/2}$ and $5d_{52}$ SCF nodeless atomic spinors (Table 2). It is noted that if in the process of forming a pseudospinor the original DF spinor is modified from its exact form from some match point inward toward the nucleus, then its behavior in the outer core region, which possesses valence-like properties, can be changed. The nodeless valence spinors, on the other hand, exhibit properties that closely reproduce the behavior of valence electrons as they penetrate the outer core region since they are defined in a self-consistent field manner in atomic calculations in which the outer core electrons are explicitly represented.

To demonstrate that these nonlocal effects are properly represented in the NV RECP, calculations were performed on the InH and InCl molecules. The two-component spinor basis sets given in Table 1 and the three RECPs discussed above were used in SCF calculations on InH and InCl in the context of $\omega\omega$-coupling.[11] (It is noted that the $5p_{1/2}$–$5p_{3/2}$ spin–orbit coupling in In is 2129 cm^{-1}, as computed using the SC RECP, in comparison with the DF value of 2147 cm^{-1}.[8] It is further noted that the use of single-determinant Hartree–Fock representations in $\omega\omega$-coupling leads to erroneous ground-state results due to the necessity for a multiconfiguration SCF treatment to ensure proper $p_{1/2}$–$p_{3/2}$ mixing.[12]) Results of $\omega\omega$-coupling SCF calculations on InH are given in Table 4. The calculations reported here are constrained as pure jj-coupling LCASs[11] for purposes of comparison to the native numerical RECPs. The ground-state molecular spinor (MS) configuration of InH is [1(1/2)^{2}2(1/2)^{2}1(3/2)^{2}2(3/2)^{2}1(5/2)^{2}3(1/2)^{2}4(1/2)^2] with the 10 In 4d electrons explicitly represented by the 1(1/2), 2(1/2), 1(3/2), 2(3/2), and 1(5/2) MSs for the SC and SC(F) RECP calculations (Table 4). For a proper direct comparison to VLC RECP and NV RECP results, the second column [SC(F) RECP] of Table 4 presents results due to freezing the three lowest-lying MSs of InH at their atomic (unperturbed) $4d_{3/2}$ and $4d_{5/2}$ forms. The SC(F) RECP results, while

retaining the 4d electrons explicitly, ensure that only the nonlocal effects are calculated since the outer core is constrained from undergoing a self-consistent field relaxation. It is these results that should be reproduced by the molecular SCF calculations using a large-core pseudopotential derived from the same all-electron numerical DF wave functions for In and In$^+$, provided, of course, that direct relativistic effects among the $4d_{3/2}$ and $4d_{5/2}$ electrons do not appreciably affect molecular properties. This is expected to be a valid assumption for indium. Experimental values for spectroscopic constants are also shown in Table 4 (for purposes of reference only). The calculations presented here were done at the SCF level of theory and suffer the expected shortcomings due to the neglect of the effects of electron correlation and intermediate angular momentum coupling.[12]

The MS (orbital) energies shown in Table 4 are generally in good agreement for all four calculations. The three lowest-energy MSs correspond to the 4d subshell electrons in the SC RECP calculations. It is seen that freezing these MSs using the $4d_{3/2}$ and $4d_{5/2}$ atomic spinors leads to, at most, an error of 2 mhartrees, indicating that the direct participation of the 4d subshell in the bonding in InH is nearly negligible at the Hartree–Fock level of approximation. However, while the effect of freezing the inner MSs leads to only a 0.02 D change in the dipole moment and a 4 cm^{-1} increase in the harmonic frequency, it results in an appreciable 0.02 Å increase in the bond distance. This indicates that an analysis based solely on the energy is not sufficient to determine the participation of the outer core electrons in bonding.

When the 10 4d electrons are included as part of the core, Hartree–Fock calculations using the resulting VLC RECP should lead to molecular properties that agree with the SC(F) RECP results. As seen in Table 4 the VLC RECP derived using shape-consistent pseudospinors[8] shows an increase of 0.17 D in the magnitude of the dipole moment and a shortening of the bond length by 0.05 Å in comparison with the SC(F) RECP results. This behavior is consistent with that observed for InH by Leininger and Stoll[13] in which a SC RECP and a VLC RECP based on the energy fitting method of Dolg et al.[14] were used. They calculated values of 1.870 Å, 1510 cm^{-1}, and −0.56 D for the bond length, harmonic frequency, and dipole moment, respectively, using a 36-core-electron treatment in which the $n = 4$ shell was held frozen at SC(F) RECP. These values compare favorably with our SC(F) RECP results, which are given in Table 4. In addition results of 1.837 Å, 1510 cm^{-1}, and −0.56 D for these properties were obtained by Leininger and Stoll using a three-valence-electron RECP, consistent with our VLC RECP results shown in Table 4. When the spin–orbit averaged RECP[8] is used, we obtain values of 1.864 Å, 1527 cm^{-1}, and −0.40 D, respectively, for the SC(F) averaged RECP (ARECP) and 1.811 Å, 1519 cm^{-1}, and −0.57 D, respectively, for the NVS ARECP, which compare directly with the values obtained by Leininger and Stoll.[13] Although the bond length is somewhat longer, the fact that their SC value exceeds their SC(F) RECP by 0.033 Å provides independent evidence that VLC RECPs yield values that are consistently too short. It is also worth noting that this phenomenon is observed both in the present pseudospinor-based RECP procedure and in that of Dolg et al.,[14] in which ab initio DF energies for a manifold of states are fitted to an analytic form comprised of Gaussian-type functions.

NODELESS VALENCE (PSEUDO)SPINORS

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Table 5. InCl LCAS-MS SCF Results[a]

property	SC	VLC	NV	exptl[b]
E_{val}[c]	−71.5376	−2.3859	−2.3814	
$1\epsilon_{1/2}$[d]	−1.041	−1.034	−1.030	
$2\epsilon_{1/2}$	−0.504	−0.507	−0.504	
$3\epsilon_{1/2}$	−0.428	−0.426	−0.423	
$4\epsilon_{1/2}$	−0.335	−0.339	−0.336	
$1\epsilon_{3/2}$	−0.425	−0.423	−0.420	
δ_{Cl}[e]	−0.55	−0.55	−0.60	
ω_e[f]	320	321	317	384
$\omega_e x_e$[g]	1.3	1.7	1.6	1.5
R_e[h]	2.480	2.425	2.486	2.321

[a] Molecular self-consistent field results in the context of the indicated RECP and two-component spinor basis set (Table 1). [b] Huber, K. P., Herzberg, G. *Molecular Structure and Molecular Spectra. IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979. [c] Total valence electron energy (hartrees) at the calculated R_e. [d] Molecular spinor energies (hartrees) at the calculated R_e. (Higher-energy MSs corresponding to outer core spinor subshells are omitted.) [e] Mulliken net charge at the calculated R_e. [f] Harmonic frequency (cm^{-1}). [g] Anharmonicity constant (cm^{-1}). [h] Equilibrium bond length (Å).

Table 6. Am^{2+} Atomic Spinor Energies (au)

(pseudo)-spinor	DF (0 core electrons)	SC (68 core electrons)	NV (78 core electrons)	NV (86 core electrons)	NV (92 core electrons)
$5d_{3/2}$	−5.51	−5.52			
$5d_{5/2}$	−4.91	−4.91			
6s	−2.72	−2.74	−2.73		
$6p_{1/2}$	−1.90	−1.93	−1.90		
$6p_{3/2}$	−1.41	−1.42	−1.42		
$5f_{5/2}$	−0.84	−0.85	−0.84	−0.84	
$5f_{7/2}$	−0.73	−0.73	−0.73	−0.73	−0.74

Table 7. $AmCl^{2+}$ Equilibrium Bond Lengths

calculation	Am RECP	R_e (Å)	calculation	Am RECP	R_e (Å)
SCF[a]	SC(78)	4.56	SCF[a]	NV(86)	4.59
SOCI[b]	SC(78)	4.50	SCF+CVPP[c]	NV(86)	4.52
SCF[a]	VLC(86)	4.23	SOCI+CVPP[d]	NV(86)	4.49

[a] Self-consistent field calculation using spin−orbit averaged Am and Cl RECPs. [b] Spin−orbit configuration interaction calculation (see the text). [c] SCF calculation including a relativistic CVPP (see the text). [d] SOCI calculation including a relativistic CVPP (see the text).

The remaining InH four-valence-electron calculation shown in Table 4 is based on the NV RECP, in which the nodeless valence spinors derived in atomic SCF calculations were used to generate the pseudopotential. The dipole moment is seen to have decreased to within 0.05 D of the SC(F) RECP result, while the bond length agrees with it to 0.001 Å (Table 4). This agreement clearly shows that the nonlocal effects that are misrepresented in the VLC RECP are faithfully propagated from the SC RECP atomic wave function (where the outer core electrons are treated explicitly) into the NV RECP.

Results for InCl, a case where RECPs are resident on more than a single atom, are shown in Table 5. The RECP for chlorine is also of the LECP form with 10 electrons defined as core and the seven 3s and 3p electrons as valence.[15] The calculations show the same trend as was observed in InH. The MS energies are comparable for the SC, VLC, and NV results, as are the spectroscopic constants. (In this instance we chose to compare to the SC calculation as opposed to carrying out a restricted SC(F) since the effects of relaxation of the 4d subshell were noted in the InH study.) The shortening of R_e by 0.55 Å in the VLC RECP calculation is, again, fully recovered in the NV RECP calculation, with the additional lengthening of 0.006 Å attributable to the SC(F)/SC relaxation effect. Therefore, there are no two-center indirect effects on the bond distance, and the shortening observed on going from the SC RECP to the VLC RECP is due to the incorrect accounting for nonlocal effects of the $4d_{3/2}$ and $4d_{5/2}$ ASs in the VLC RECP. These results are also in good agreement with the SCF results of Schwerdtfeger et al., who employed an RECP that placed 28 electrons in the core and treated the remaining 21 electrons explicitly as valence electrons.[7]

As a further test of the accuracy of the nodeless valence (pseudo)orbital approach, RECPs were derived for Am (Z = 95) in which SC RECPs based on core-electron spaces of 68[16] and 78[17] electrons were used in atomic SCF calculations employing large two-component spinor basis sets of Slater-type functions (STFs) to derive NVSs and NVPSs. These spinors were, in turn, used to derive a new RECP for Am in which 86 and then 92 electrons were defined as the core space. The spinors that describe the remaining valence electrons in SCF calculations for Am^{2+} were then represented

using STFs. The results of the study are compared with all-electron numerical DF results in Table 6.

It is noted that, in the respective cases of DF, RECP-68, RECP-78, RECP-86, and RECP-92, the number of electrons treated explicitly in the SCF calculations on Am^{2+} are, respectively, 95, 25, 15, 7, and 1. In terms of the scaling of the calculations, as determined at the SCF level by the number n of STOs in the two-component spinor basis set, the number of two-electron integrals is $O(n^4)$ for the various RECPs. The RECP-based calculations shown in Table 6 correspond to basis sets comprised of 73, 49, 28, and 4 two-component STFs, respectively. The SCF scaling reduces as 2.8×10^7, 5.8×10^6, 6.1×10^5, and 2.6×10^2, respectively. The scaling for integral transformations is $O(n^5)$, and various methods for including electron correlation [CI, MP, CCSD(T), etc.] can degrade as poorly as $O(n^7)$. (Although the use of RECP-92 represents Am^{2+} as a one-electron atom, molecules and complexes will, of course, require the accurate treatment of the valence electrons of the bonded atoms and ligands.)

SCF calculations using spin−orbit averaged RECPS[8,17] were carried out on $AmCl^{2+}$. Results for the equilibrium bond distance due to calculations employing RECPs corresponding to core spaces comprised of 78 (SC RECP) and 86 electrons (VLC RECP) were 4.56 and 4.23 Å, respectively, as shown in Table 7.[18] In the SC and VLC RECPs the LEPC method was modified using the procedure of Wildman et al. to improve the representation of the f pseudospinors in the core region.[20] When the corresponding NV RECP is used, a bond length of 4.59 Å results (with the additional 0.03 Å increase attributable to the SCF relaxation of the outer core ASs in the SC RECP calculation) as can be seen in Table 7. This shortening when using the LC RECP (due to the incorporation of the additional eight electrons into the outer core) and then recovery of the nonlocal error upon rederiving the RECP using NVPSs and NVSs reaffirm the importance of using NVPSs and NVSs when deriving VLC RECPs. As was explained previously, some of the ASs used to derive the NV RECP are nodeless and some have one node. In the latter case, the node is removed to produce a NVPS. To emphasize

this point, namely, that both NVSs and NVPSs are used to derive a NV RECP, the term nodeless valence (pseudo)spinor NV(P)S is used. Here, the parentheses denote that the spinor from which the RECP is generated can be either a NVS or a NVPS and emphasize that there is a distinction between the two.

The effects of core/valence polarization are especially important in many-atom systems in which VLC RECPs are employed, such as those containing americium described using either 86 or 92 core-electron spaces. As an example spin−orbit configuration interaction (SOCI) calculations[1] that included single plus double excitations relative to the SCF configuration and a relativistic core/valence polarization potential[21] were performed using the SC and NV RECPs. The results shown in Table 7 indicate that an increase in the bond distance of 0.26 Å was observed. Thus, it is imperative to incorporate both the effects of core/valence polarization and the effects of nonlocal electron repulsion phenomena since these errors are large and are of opposite sign. Both of these effects are addressed using a procedure in which the outer cores, represented currently using VLC RECPs, are permitted to undergo a self-consistent field relaxation due to the molecular environment, that is, through a geometry- and state-dependent functional called the relativistic pseudo-potential.[19] For example, the ability to incorporate six of the seven f subshell electrons in Am into the outer core leaves only three electrons that will require explicit treatment. It is seen in Table 6 that the splitting between the $5f_{5/2}$ and $5f_{7/2}$ ASs is 3 eV. For certain bonding and complexation environments, this energy separation is sufficiently large that the $f_{5/2}$ electrons can be considered as part of the outer core.

4. CONCLUSIONS

Nonlocal effects are shown in the requisite bond length increase in the NV RECP results relative to an InH molecule described with the shape-consistent VLC RECP. The NV RECP results are consistent with the analogous SC(F) RECP calculation in which the In $4d_{3/2}$ and $4d_{5/2}$ subshell spinors were held frozen in their atomic SCF form. This is attributed to a correct accounting for nonlocal effects due to outer core electrons in VLC RECPs derived from nodeless valence two-component (pseudo)spinors in a manner that involves a rigorous transformation from the SC RECP to the NV RECP.

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