Reliable Electronic Structure Calculations for Heavy Element Chemistry: Molecules Containing Actinides, Lanthanides, and Transition Metals:

Relativistic Pseudopotentionals in Accurate ab Initio Molecular Electron Structure Calculations

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Abstract

Relativistic Pseudopotentionals (RPPs) are a new form of relativistic effective core potentials (RECP) that are based on extending the usual two-space representation of atomic electrons (core and valence) to three spaces: core, outer core, and valence. The RPP has embedded within it the so-called small-core RECP, viz., one that relegates the outer core electrons to the valence space. The RPP is ultimately specified completely only at runtime and is specific to the molecular environment (geometry and electronic state). Only the smallest number of molecular valence electrons need to be treated explicitly, and can be used in any treatment of the electronic structure including DFT, CI (configuration interaction), MBPT (many body perturbation theory), coupled cluster theory (CCSD/CCSD(T)), etc. Furthermore, the one-particle basis set (orbitals or spinors) need only be sufficiently flexible to represent the valence electrons - no core or outer core basis functions are required. As the RPP formalism has only recently been developed, its implementation and application are key thrusts of this project. The enormous reduction in computational effort over all-electron and standard RECP approaches, coupled with the inclusion of relativistic and core/valence polarization and correlation phenomena, are principal advantages to using RPPs to study heavy atom complexes.

Once the implementation is complete, the use of small-core RECPs embedded within very-large-core RPPs, used in conjunction with advanced computing platforms, will permit the highly accurate ab initio treatment (including correlation, outer-core/valence polarization, and spin-orbit coupling) of systems possessing orders of magnitude more electrons than are tractable using current codes and platforms. This results in savings that scale as much as O(N**5) for the incorporation of N outer core electrons into the RPP in the context of, for example, a CCSD(T)-level calculation. For example, in the case of Am (Z=95), the reduction is from the small-core representation involving 27 valence electrons to embedding this SC-RECP into a 9-valence-electron RPP. Thus, only 9 outermost electrons must be treated explicitly, rather than 27 and for a calculation scaling as N**5, this leads to a reduction by a factor of almost 250 in computational cost. Furthermore, for certain structural studies, Am can be represented using an RPP that will enable the reduction of the number of valence electrons to as small as 3, significantly increasing this factor.

"Relativistic Pseudopotentional Incorporating Core/Valence Polarization and Nonlocal Effects", M. M. Marino, The Journal of Chemical Information and Computer Sciences, **41**, 64, 2001.

"Nodeless Valence (Pseudo)Spinors", W. C. Ermler and M. M. Marino, The Journal of Chemical Information and Computer Sciences, **41**, 77, 2001.

Relativistic Pseudopotentionals (RPPs)

RPPs are based on extending the usual two-space representation of atomic electrons (core and valence) to three spaces (core/outer core/valence).

The RPP has embedded within it the standard small-core RECP that relegates the outer core electrons to the valence space.

The RPP is ultimately calculated in its entirety at runtime and is specific to the molecular geometry and electronic state.

Only the smallest numbers of molecular valence electrons need to be treated explicitly.

The RPP can be used in any level of electronic structure theory [DFT, CI, CCSD(T), etc.].

The RPP is comprised of two parts:

$$\mathbf{F}^{\mathbf{RPP}}\,\mathbf{C} = \mathbf{SC}\boldsymbol{\varepsilon} \qquad (1a)$$

$$F_i^{RPP} = [U_i^{RECP} + H_i^{o} + \Sigma_j (J_j - K_j)] \,, \qquad (1b)$$

$$\mathbf{CU}^{\mathbf{RPP}} = \mathbf{S"}\boldsymbol{\varepsilon}\mathbf{"} - \mathbf{F'}^{\mathbf{RPP}}\,\mathbf{C_{vi}"}/\,\mathbf{C_{pvi}"} \,, \qquad (2)$$

Part 1 involves the outer core electrons and is defined in terms of that portion of the Fock matrix involving outer core two-component spinors, ϕ_i [Eq. (1a)]. The operators that define $\mathbf{F}^{\mathbf{RPP}}$ are given by Eq. (1b) and include the one-electron Hamiltonian operator H_i^{o}; one-electron coulomb and exchange operators J_j and K_j; and the small-core RECP.

Part 2 is defined by Eq. (2), where $\mathbf{CU}^{\mathbf{RPP}}$ are matrices. $\mathbf{U}^{\mathbf{RPP}}$ is associated with a set of one-electron RECP operators that operate on the valence spinors of the molecule, and **C** contains the outer core vectors. **S"** and $\boldsymbol{\varepsilon}$**"** are overlap and off-diagonal Lagrange multiplier matrices, respectively, corresponding to the valence space. $\mathbf{C_{vi}"}$ is a vector containing the coefficients of the valence basis functions, and $\mathbf{C_{pvi}"}$ is a vector corresponding to the nodeless valence pseudospinor.

Small-core RECPs embedded within very-large-core (VLC) RPPs, in conjunction with advanced computing platforms, permit the highly accurate ab initio treatment (including correlation, outer-core/valence polarization, and spin-orbit coupling) of systems possessing orders of magnitude more electrons than are tractable using current codes and platforms.

Nodeless Valence Spinors (NVS) and Pseudospinors (NVPS)

Atomic calculations using small-core (SC) RECPs explicitly treating outer core electrons form the basis for extracting two-component NVS and NVPS used to generate very large-core RPPs

1. All-electron DF wavefunction is calculated.
2. Nodes are removed from so-defined valence spinors by means of the shape-consistent pseudospinor procedure to form the SC RECP.
3. The SC RECP is used to derive NVS and NVPS.
4. These NVS and NVPS are used to derive larger core RECPs and/or RPPs.
5. Steps 3 and 4 are repeated until the very-large core RECP or RPP is achieved.

Table I. Am^{2+} (Z=95) Atomic Spinor Energies (a.u.)

PseudoSpinor	DF	SC	NV	NV	NV
Core electrons	0	68	78	86	92
$5d_{3/2}$	-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

RECPs were derived for Am *(Z*=95) in which SC RECPs based on core spaces of 68 and 78 electrons were used in atomic SCF calculations with large spinor basis sets to derive NVPS. These spinors were, in turn, used to derive new RECPs for Am in which 86, and then 92 electrons were defined as the core space. The results for the successive RECPs are shown in Table I above.

Relativistic SCF calculations[1] using spin-orbit averaged RECPS[2,3] 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 (LC RECP) were 4.56 and 4.23 Å, respectively, as shown in Table II.[4] In the SC and LC RECPs the standard method[1] was modified using the procedure of Wildman et al. to improve the representation of the f pseudospinors in the core region.[5] 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 atomic spinors in the SC RECP calculation) as can be seen in Table II. 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 re-deriving the RECP using NVPSs and NVSs reaffirm the importance of using NVPSs and NVSs when deriving LC RECPs. Some of the atomic spinors 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.

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

Calculation	Am RECP	R_e(A)	Calculation	Am RECP	R_e(A)
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]	LC(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.

[c]Self-consistent field calculation including a relativistic CVPP.

[d]Spin-orbit configuration interaction calculation including a relativistic CVPP.

The effects of core/valence polarization are especially important in many-electron systems in which LC RECPs are employed, such as those containing Am 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[6] were performed using the SC and NV RECPs. The results shown in Table II indicate that an increase in the bond distance of 0.26 A 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 here using LC RECPs, are permitted to undergo a SCF relaxation due to the molecular environment; that is, through a geometry- and state-dependent functional - the RPP. For example, the ability to incorporate six of the seven f subshell electrons in Am into the outer core leaves only three electrons that require explicit treatment. It is seen in Table I that the splitting between the $5f_{5/2}$ and $5f_{7/2}$ atomic spinors 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.

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