

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

## Relativistic Pseudopotentials in Accurate *ab Initio* Molecular Electronic Structure Calculations

Scientific Discovery through Advanced Computing (SciDAC) Project: BES  
Computational Chemistry

M. M. Marino and W. C. Ermler, University of Memphis, Department of Chemistry

### Abstract

It is now possible to calculate many properties including the energetics (total bond dissociation energies or heats of formation) of molecules containing light elements to high accuracy by using correlation-consistent basis sets, coupled cluster theory and including additive corrections for core-valence and relativistic effects and careful treatment of the zero point energy. We propose to develop software for *ab initio* electronic structure calculations based on molecular orbital theory and density functional theory with the proper treatment of relativistic effects to study complexes of heavy elements in order to assist in understanding and predicting the chemistry of the actinides, lanthanides, and heavy transition metals, molecules critical to DOE missions including environmental management. The proposed work will focus on the development of these electronic structure methods and their implementation in software on advanced massively parallel processor (MPP) computer architectures capable of multi-tens of teraflops to petaflops. The core of the software will be developed within the NWChem and Columbus software suites. We propose to make the software broadly available so that other scientists can use these tools to address the complex environmental problems facing the Department of Energy's nuclear production sites as well as other waste sites in the Nation. Our implementation of relativistic quantum chemical methods for massively parallel computers will enable us to simulate the behavior of heavy-element compounds at the same type of level currently available for light-element compounds. In addition, this work will enable us to provide better methods for benchmarks of the additive energetic schemes currently available for light atom compounds. The theoretical and computational methodology so developed will be an invaluable supplement to current, very expensive experimental studies of the actinides, lanthanides, and radioactive heavy transition metal elements, allowing limited experimental data to be extrapolated to many other regimes of interest. The new tools can be used to study, for example, the interaction of actinides with organic complexing agents present in tank wastes and with natural aqueous systems (carbonates) in order to better understand their fate and transport in the environment, as well as interactions with new materials such as phosphates and amides for the design of innovative *in situ* remediation technologies and separation materials. In addition, the proposed work will allow scientists to tackle the complexity of excited states in heavy element compounds especially those comprised of actinide, lanthanide, and heavy transition metal atoms.

This final report summarizes research outcomes from a project funded under the Scientific Discovery through Advanced Computing (SciDAC) Program through the Basic Energy Sciences Chemical Sciences Program of the Office of Science of the U. S. Department of Energy. The original grant was for a 3-year project. Because of delays in processing award following the relocation of the principal investigators it was reduced to a 2-year project. Although the award was based on the original proposal and no changes in the research plan were requested the project was reduced to having a 2-year duration (January 1, 2002 through December 31, 2004). An 8-month supplemental award was granted by BES at the end of the 2-year project period (January 1, 2004 through August 31, 2004). This extension covered the salary of the PI through an additional Spring academic term. An additional 6-months salary for the PI was granted to the PI to cover her salary for collaboration involving the companion SciDAC project at Ohio State University, Russell M. Pitzer (PI), Department of Chemistry (September 1, 2004 through February 28, 2005).

Realizing the full potential of terascale computing requires not only the use of next-generation hardware coupled with software specifically developed to make full use of such advanced platforms, but it also requires that the software employed incorporate the latest theoretical developments that will guarantee high accuracy and tractability for the systems of interest. In many instances, the tractability of a calculation depends on the number of electrons that must be treated explicitly, and this relationship holds even if the most highly advanced hardware platform is employed. Consequently, the purpose of this project was to develop the computational methodology needed to treat molecules that contain heavy elements (i.e., atoms that contain large numbers of electrons) at an accuracy comparable to what can be achieved for molecules containing first and second row atoms (e.g. carbon, which contains only six electrons) and to implement this technology in high performance software that is portable and scalable on massively parallel computer systems.

The number of electrons treated explicitly may be reduced by realizing that not all electrons are involved in chemical bonding. Since only the valence (bonding) electrons must be treated explicitly, the rest of the electrons, which are labeled “core”, can be represented by a relativistic effective core potential (RECP). For example, americium (Am) contains 95 electrons, but the use of an RECP to represent the core electrons of Am reduces this number to 27, which represents over a 70% reduction in the number of electrons requiring explicit treatment for this atom alone. Despite such an impressive reduction, the valence space of Am actually contains only 9 electrons and, for certain structural studies, the valence space of Am<sup>+2</sup> can be described using only one electron. The use of a 9- or 1-electron valence space RECP for Am or Am<sup>+2</sup>, however, would result in significant errors. While the RECP (as well as all other pseudopotential methods) relies on the principle of core/valence separability, nature actually contains a third type of electronic region, labeled “outer core” comprised of electrons that while affected by chemical bonding do not participate directly in the process. Since no pseudopotential method to date accurately describes the outer core, these electrons are routinely relegated to the valence region for explicit treatment, resulting in either

unnecessary complexity or computational intractability, even if state-of-the-art hardware platforms are used along with software specifically optimized for such platforms.

In this context, we have developed a relativistic pseudopotential (RPP) for use in *ab initio* molecular electronic calculations. The RPP is a new form of RECP that is based on extending the usual two-space representation of atomic electrons (core and valence) to three spaces (core, outer core and valence), thus requiring only the smallest number of molecular electrons to be treated explicitly. The use of very large core RPPs in conjunction with advanced computing platforms will permit the highly accurate *ab initio* treatment of systems possessing orders of magnitude more electrons than are tractable using current codes and platforms. For example, an RECP would reduce the number of explicitly treated electrons in Am from 95 to 27. However, a RPP would reduce this number to 9. For electronic structure calculations scaling as  $N^5 - N^7$  (which is normal for these types of systems), where N is the number of valence electrons, this leads to a reduction of 250 - 2000 in computational cost. In other words, a calculation that would require 2000 hours of computer time to complete with a RECP could be completed in approximately one hour with an RPP.

Affiliated SciDAC researchers were R. M. Pitzer, B. E. Bursten and I. Shavitt of The Ohio State University. This group expanded and enhanced the Columbus suite of electronic structure codes for efficient parallel computations of electronic wave functions for polyatomic systems containing heavy elements in which the core and outer core electrons are represented by RECPs and RPPs. New RECPs for use by this group were developed by the PIs. Additionally we collaborated with J. L. Tilson, Center for Computational Research (CCR), SUNY, Buffalo and A. F. Wagner and R. Shepard of ANL using our parallel spin-orbit CI modification of Columbus for applications to  $\text{AmCl}^+$ .

We carried out calculation for the individual elements, initially Am and Cl. We utilized a two-component basis set representation of small-core RECP-based atomic wave functions needed to generate an RPP, as opposed to the numerical, all-electron wave functions used in the generation of RECPs. We also generated the angular momentum projection operators to be associated with the RPPs. Unlike their RECP counterparts, these operators are not developed in the context of the Wigner-Eckart theorem, thus allowing for the symmetry-breaking that takes place when outer core electrons polarize in response to bonding. This results in operators containing additional angular degrees of freedom, as opposed to the two angular-component-based operators of the RECPs.

## Summary of Results

1. Derived a formalism by which core/valence correlation is included in the RPP procedure via a multi-configuration self-consistent field wave function.

$$\Phi_{\text{MCSCF}} = \sum_{i=1}^n C_i \Phi_i \quad (1)$$

where  $n$  is the number of configurations,  $C_i$  is the coefficient of the  $i^{\text{th}}$  configuration and  $\Phi_i$  is the  $i^{\text{th}}$  configuration function.

Also,

$$|\Phi_{\text{MCSCF}}\rangle = C_0|\Psi_0\rangle + \sum_{\text{mr}} C_{\text{m}}^{\text{r}} |\Psi_{\text{m}}^{\text{r}}\rangle + \sum_{\text{mnrs}} C_{\text{mn}}^{\text{rs}} |\Psi_{\text{mn}}^{\text{rs}}\rangle + \sum_{\text{mnorst}} C_{\text{mno}}^{\text{rst}} |\Psi_{\text{mno}}^{\text{rst}}\rangle + \sum_{\text{mnoprstu}} C_{\text{mnop}}^{\text{rstu}} |\Psi_{\text{mnop}}^{\text{rstu}}\rangle + \dots \quad (2)$$

where

$$\Psi_i = A[(\phi_{\text{m}}\phi_{\text{n}}\phi_{\text{o}}\dots\phi_{\text{q}})(\phi_{\text{r}}\phi_{\text{s}}\phi_{\text{t}}\dots\phi_{\text{z}})]. \quad (3)$$

Here, the subscripts  $m$  through  $q$  denote valence orbitals and the subscripts  $r$  through  $z$  denote the virtual orbitals, and

$$\phi_i = \sum_{\text{p}} C_{\text{pi}} \chi_{\text{p}} \quad (4)$$

where  $\chi_{\text{p}}$  denote valence basis functions, respectively.

Eq. (2) shows the contributions to the total MCSCF wave function from the root configuration and all single, double, triple, quadruple, etc. excitations.

Eq. (3) shows the orbitals comprising each configuration. In this equation, the valence orbitals are derived solely from valence basis functions and can be either singly or doubly occupied. The virtual orbitals, which, by definition, are not occupied are derived solely from valence basis functions and, therefore, have no contributions from the outer core basis functions.

The contribution from the outer core orbitals is brought into the calculation when that part of the relativistic pseudopotential (RPP) operator that represents the outer core/valence interactions operates on the wave function of Eq. (2):

$$cU^{\text{RPP}}|\Phi_{\text{MCSCF}}\rangle = cU^{\text{RPP}} [C_0|\Psi_0\rangle + \sum_{\text{mr}} C_{\text{m}}^{\text{r}} |\Psi_{\text{m}}^{\text{r}}\rangle + \sum_{\text{mnrs}} C_{\text{mn}}^{\text{rs}} |\Psi_{\text{mn}}^{\text{rs}}\rangle + \sum_{\text{mnorst}} C_{\text{mno}}^{\text{rst}} |\Psi_{\text{mno}}^{\text{rst}}\rangle + \sum_{\text{mnoprstu}} C_{\text{mnop}}^{\text{rstu}} |\Psi_{\text{mnop}}^{\text{rstu}}\rangle + \dots] \quad (5)$$

where  $cU^{\text{RPP}}$  is the RPP operator and  $c$  contains the set of coefficients corresponding to the outer core basis functions.

From Eq. (4) it is clear that the coefficients corresponding to the valence basis functions are contained in  $\Psi_i$  and, therefore, in  $\Phi_{\text{MCSCF}}$ , also, while Eq. (5) shows how the set of outer core coefficients participate in the calculation even though no outer core basis functions appear in either the valence or the virtual spaces. Consequently, both the set of coefficients corresponding to the basis functions and to the configuration functions may be variationally optimized. However, although the outer core functions participate in the self-consistent optimization, they do not appear in the valence space. Thus, these basis

functions do not participate in the excitation process, only in the optimization one. In other words, they relax in the field of valence excitations.

It is noted that the outer core and valence orbitals comprise an orthonormal set. Therefore, although only the valence orbitals participate in electronic excitation, the coefficients corresponding to all of the orbitals must be self-consistently optimized in the MCSCF procedure.

2. Derived an angular momentum projection operator for use with RPP-based MCSCF-CI procedures.

Analogously to the standard Lee/Ermler/Pitzer/Christiansen RECP method,  $cU^{RPP}$  may be expressed as products of angular projection operators and radial functions:

$$c_{lj} U_{lj}^{RPP} = \sum_l \sum_{j=|l-1/2|}^{l+1/2} \sum_{m=-j}^j c_{lj} U_{lj}^{RPP} (r) |l j m\rangle \langle l j m| \quad (6)$$

This form is accurate for describing core-valence polarization phenomena, which can be studied at the Hartree-Fock level of theory.

However, it is not sufficient for use in post-SCF procedures.

RECPs are generally derived using the Wigner–Eckart theorem, i.e., atomic spherical symmetry is assumed to be maintained and the core angles are integrated out during the derivation. Projection operators are then used to allow for the breaking of atomic spherical symmetry in molecular calculations, yielding a form nearly identical to that of Eq. (6):

$$U_{lj}^{RPP} = \sum_l \sum_{j=|l-1/2|}^{l+1/2} \sum_{m=-j}^j U_{lj}^{RPP} (r) |l j m\rangle \langle l j m| \quad (7)$$

Operating on the angular part of the valence orbitals with either the operator of Eq. (6) or of Eq. (7) yields integrals of the type

$$\langle (l j m)_v (l j m)_c | (l j m)_v (l j m)_c \rangle \quad (8)$$

It is appropriate to use this form of angular momentum projection operator with RECPs because the purpose of RECPs is to describe the atomic core orbitals, and these orbitals really do maintain atomic spherical symmetry. However, RPPs are derived for the purpose of describing the outer core region, and, since these orbitals polarize, the atomic spherical symmetry is broken.

To address this problem, angular momentum projection operator associated with RPPs are developed without employing the Wigner-Eckart theorem in the process.

This may be done as follows:

The repulsion operator between a core and a valence electron may be expressed (using the Neumann expansion) as

$$1/r_{cv} = \sum_l \sum_{m=-l}^l [(-1)^m / (1+|m|)!] Y_{lm}^*(\theta_v \phi_v) [(r_c^l / r_v^{l+1}) Y_{lm}(\theta_c \phi_c) + (r_v^l / r_c^{l+1}) Y_{lm}(\theta_c \phi_c)] \quad (9)$$

If the Wigner-Eckart theorem is not used, then the outer angles remain in the derivation and the following types of integrals result:

$$\langle (l_j m_j)_v (l_j m_j)_c | (l_j m_j)'_v (l_j m_j)'_c | (l_j m_j)_v (l_j m_j)_c \rangle \quad (10)$$

Where  $(l_j m_j)'_v$  and  $(l_j m_j)'_c$  arise from the Neumann expansion of the operator  $1/r_{cv}$ . The integral of Eq. (10) involves more degrees of freedom than that of Eq. (7). Consequently, it is able to describe complex polarization phenomena such as those described using post-Hartree-Fock treatments.

3. Carried out benchmark studies of very-large-core/valence space separations in  $\text{AmCl}^{2+}$  to investigate the suitability of the electrons in a given subshell to be labeled outer core and thus be described by an RPP.

Relativistic SCF calculations using spin-orbit averaged RECPs were carried out on  $\text{AmCl}^{2+}$ . 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 I. 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 I. 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 I.  $\text{AmCl}^{2+}$  Equilibrium Bond Lengths

Calc.	Am RECP	$R_e(\text{Å})$	Calc.	Am RECP	$R_e(\text{Å})$
SCF <sup>a</sup>	SC(78)	4.56	SCF <sup>a</sup>	NV(86)	4.59
SOCI <sup>b</sup>	SC(78)	4.50	SCF+CVPP <sup>c</sup>	NV(86)	4.52
SCF <sup>a</sup>	LC(86)	4.23	SOCI+CVPP <sup>d</sup>	NV(86)	4.49

<sup>a</sup>Self-consistent field calculation using spin-orbit averaged Am and Cl RECPs.

<sup>b</sup>Spin-orbit configuration interaction calculation.

<sup>c</sup>Self-consistent field calculation including a relativistic CVPP.

<sup>d</sup>Spin-orbit configuration interaction calculation including a relativistic CVPP.

### **Publications**

Tilson, J. L.; Naleway, C.; Seth, M.; R. Shepard, R.; Wagner, A. F.; Ermler, W. C. *An ab Initio Study of AmCl<sup>+1</sup>: f-f Spectroscopy and Chemical Binding*. J. Chem. Phys. 121, 5661-5675 (2004).

Ermler, W. C. *Relativistic effective core potential and spin-orbit coupling operator for the erbium atom*. Derived for use by the Ohio State University SciDAC Project team of PI Russell M. Pitzer.