



Generally contracted valence–core/valence basis sets for use with relativistic effective core potentials and spin–orbit coupling operators

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ABSTRACT

A procedure for structuring generally contracted valence–core/valence basis sets of Gaussian-type functions for use with relativistic effective core potentials (gcv-c/v-RECP basis sets) is presented. Large valence basis sets are enhanced using a compact basis set derived for outer core electrons in the presence of small-core RECPs. When core electrons are represented by RECPs, and appropriate levels of theory, these basis sets are shown to provide accurate representations of atomic and molecular valence and outer-core electrons. Core/valence polarization and correlation effects can be calculated using these basis sets through standard methods for treating electron correlation. Calculations of energies and spectra for Ru, Os, Ir, In and Cs are reported. Spectroscopic constants for RuO²⁺, OsO²⁺, Cs₂ and InH are calculated and compared with experiment.

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1. Introduction

A critical problem that must be addressed in calculations of many-electron wave functions is the prediction of accuracy. All methods based on linear combinations of atomic orbitals to form molecular orbitals (LCAO–MO) in the context of Hartree–Fock (HF) and subsequent post-HF procedures such as configuration interaction (CI), many-body perturbation theory and its variants including the state-of-the-art coupled cluster (CC) methods, and density functional theory (DFT), must be assessed. The use of primitive Cartesian Gaussian-type functions (GTFs), most often incorporating some form of contraction (CGTFs) based upon atomic self-consistent field (SCF) wave functions and upon molecular calculations, often termed correlation-consistent basis sets, have been studied extensively [1–3]. The importance of choosing basis sets that are both carefully optimized and contain sufficient numbers of functions cannot be overstated. Furthermore, once this basis set has been established, post-HF procedures must address the additional concerns of the size and quality of the subsequent one-electron SCF or multiconfiguration (MCSCF) MO basis set and the set of MO electron configurations (in CI methods) or levels of excitations (in CC methods) that define many-electron wave function for the desired electronic states, including issues of size-consistency [1].

The exact solution for three methods mentioned above, MCSCF–MO, CI and CC, are, of course, formally known and have been effec-

tively achieved computationally in a number of benchmark studies [4,5]. These computations for a bound atom or molecule correspond to denumerably infinite numbers of basis functions, MO electron configurations and orders of perturbation theory. Of course, MOs are unnecessary in the case of full-CI and it is only required that the basis set be rendered orthonormal [4]. It is demonstrated here that the incorporation of relativistic effective core potentials (RECPs), including their corresponding spin–orbit coupling (SO) operators derived from all-electron *ab initio* Dirac–Fock atomic wave functions for average-energy-of-configuration electronic states and the concomitant generally contracted valence–core/valence (gcv-c/v) CGTF basis sets can provide the flexibility to carry out accurate calculations of electronic structures and spectra.

2. Method

Generally, for molecular systems containing heavy elements, angular momentum coupling is not well defined using wave functions that are eigenfunctions of the operator S^2 and of irreducible representation operators of the molecular point group. A significantly better description uses wave functions that are eigenfunctions of the total molecular angular momentum operator J^2 and one of the symmetry types of the molecular double group [6,7]. Also, even for light element systems, the fine structure of spectra is not revealed unless spin–orbit coupling phenomena are included.

Procedures based on the use of RECPs derived from all-electron *ab initio* numerical DF atomic wave functions afford the ability to

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reduce the number of electrons that must be treated explicitly to a small enough number that, in many instances, large-basis-set CI and CC calculations incorporating spin-orbit coupling and other relativistic effects become feasible [8–11]. RECPs and Gaussian basis sets for representing valence electrons have been reported for all of the elements from Li through element 118 by Christiansen, Ross, Ermler and co-workers [12–18]. The RECP method is grounded in the fundamental tenet that atomic core and valence electrons can be formally distinguished and treated rigorously from first principles as identifiable sets. In addition to distinguishing between core and valence electrons, the effects of relativity must also be considered, especially for heavy elements. The high nuclear charge in heavy element systems leads to tightly bound inner shell electrons whose confinement raises their average kinetic energy such that relativistic effects become important. Relativistic effects on the valence space electrons include (1) radial contraction and energetic stabilization of s and $j = l - 1/2$, $l > 0$, atomic orbitals often leading to bond shortening; (2) radial expansion and energetic destabilization of $j = l + 1/2$, usually with somewhat smaller chemical effects; and (3) relativistic spin-orbit splitting of p , d , f and higher orbital angular momentum orbitals into sublevels with different energies [8]. As first shown by Lee et al. [19] the use of Dirac-Fock-based (DF) RECPs permits the incorporation of these effects into molecular electronic structure calculations, and at the same time reduces the problem such that only the valence electrons require an explicit theoretical treatment in the context of valence-subshell only basis sets. RECPs were based on shape-consistent two-component Nodeless Pseudospinors (NPSs) extracted from all-electron numerical DF atomic wave functions of the form defined by Lee, Ermler, Christiansen and Pitzer (LECP) [19,20].

To clarify the context of the gcv - c/v -RECP basis set approach, necessarily utilized in the context of RECPs a short formal description of the latter is given. It is noted that the procedure can be used to combine basis sets for other forms of ECPs [9,11] and large CGTF basis sets [2,3]. The LECP RECPs are defined using shape-consistent NPSs [20] extracted from numerical two-component DF atomic spinors [19]. NPSs are then used to define individual RECPs in the context of jj -coupling that are expressed as

$$U_{lj}^{\text{RECP}} = U_{lj}^{\text{RECP}}(r) + \sum_{l=0}^{L-1} \sum_{j=l-\frac{1}{2}}^{l+\frac{1}{2}} \sum_{m=-j}^j [U_{lj}^{\text{RECP}}(r) - U_{lj}^{\text{RECP}}(r)] |ljm\rangle \langle ljm| \quad (1)$$

In Eq. (1) the projection operators $|ljm\rangle \langle ljm|$ dictate that U_{lj}^{RECP} must be used subsequently in the context of a basis set of two-component Dirac spinors. U_{lj}^{RECP} refers to the so-called residual RECP term, where L and J are normally taken as one larger than the largest angular momentum quantum numbers of the core electrons. The RECPs can be recast into the form of angular momentum averaged relativistic effective core potentials (ARECPs) that may be used in the context of standard nonrelativistic electronic structure procedures based on atomic LS-coupling. An important consequence of this averaging is the formation of a spin-orbit operator [6,7].

$$U_l^{\text{ARECP}} = U_l^{\text{ARECP}}(r) + \sum_{l=0}^{L-1} \sum_{m=-1}^1 [U_l^{\text{ARECP}}(r) - U_l^{\text{ARECP}}(r)] |lm\rangle \langle lm| \quad (2)$$

with

$$U_l^{\text{ARECP}} = (2l+1)^{-1} [lU_{l-1/2} + (l+1)U_{l+1/2}] \quad (3)$$

This averaging procedure leads to the spin-orbit operator

$$H^{\text{SO}} = S \cdot \sum_1^{L-1} [2/(2l+1)] \Delta U_1(r) \sum_{m=-1}^1 |lm\rangle \langle lm| \mathbf{1} |lm\rangle \langle lm| \quad (4)$$

where S and l are the spin and orbital angular momentum vector operators and

$$H_l^{\text{SO}} = [2/(2l+1)] \Delta U_1(r) \quad (5)$$

With

$$\Delta U_l(r) = U_{l-\frac{1}{2}} - U_{l+\frac{1}{2}} \quad (6)$$

The Hamiltonian matrix relevant to valence-electron-only atomic and molecular systems is constructed in terms of matrix elements involving U^{ARECP} and H^{SO} and LCAO-MO-based determinantal wve function for valence electrons defined through standard LS-coupling SCF or MCSCF procedures.

The Hamiltonian operator for valence electrons i and j and atoms c is, in a.u.,

$$H^{\text{val}} = \sum_i \left(-\frac{1}{2} \nabla_i^2 - \sum_c Z_c/r_{ci} \right) + \sum_{i>j} 1/r_{ij} + \sum_c (U_c^{\text{ARECP}}) \quad (7)$$

The resulting (MC)SCF wave functions are eigenfunctions of point-group irreducible representation operators and the total spin angular momentum operators. Thus, existing *ab initio* molecular structure codes effectively form a framework to calculate LCAO-MO wave functions.

Pitzer and Winter used a form of the LECP operator H^{SO} in the context of double group theory to define a Spin Orbit Configuration Interaction (SOCl) procedure that leads to molecular wave functions with the proper intermediate angular momentum coupling for an electronic state [7]. In their representation the spin-orbit operator of Eq. (4) is expressed in terms of orbital angular momentum projection operators

$$O_1 = \sum |lm_i\rangle \langle lm_i| \quad (8)$$

where the jj -coupling required by the RECP of Eq. (1) sums over j to a projection operator O_l

$$\sum O_j = \sum |ljm_j\rangle \langle ljm_j| \quad (9)$$

This permits the expression of H^{SO} to be of the well-known form of a radially dependent function times the inner product of the orbital and spin angular momentum vector operators, $\xi_l(r) \mathbf{l} \cdot \mathbf{s}$ [see Eq. (4)]. The working form is then expressed in terms of a sum over only the orbital angular momentum quantum number.

$$H^{\text{SO}} = \sum O_l \xi_l(r) \mathbf{l} \cdot \mathbf{s}_l \quad (10)$$

These operators in numerical form are typically re-expressed as expansions in Gaussian-type functions (GTFs) to facilitate their use in molecular electronic structure codes that employ GTF basis sets. That is, the RECP of Eq. (1), ARECP of Eq. (2) and SO operator of Eq. (10) can all be expressed as expansions in GTFs as

$$V(r) = \sum_i C_i r^{n_i} e^{-r^2 \alpha_i} \quad (11)$$

where the operator V represents U_{lj}^{RECP} of Eq. (1), U_l^{ARECP} of Eq. (2), and H_l^{SO} of Eq. (5).

Although chemical intuition supports the concept of core/valence separation, it is well known that for many elements the polarization/correlation interactions between the outermost electrons and those lying in the subshells of next lower principal quantum number must be taken into account [21]. Interatomic interactions involving such phenomena can be large [22] and must be included in accurate treatments of polyatomic systems. A method due to Christiansen [23] which is an *ab initio* extension of a procedure due to Müller et al. [24] defines a core polarization potential operator $V^{\text{CVPP}}(r)$. This operator is derived from valence electron calculations employing RECPs that include explicitly the outer and next innermost shells of electrons. It includes the effects of one- and two-electron core-valence correlation interactions and core-polarization. The CVPP, and its complement in jj -coupling

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