

SHAPE-CONSISTENT RELATIVISTIC EFFECTIVE POTENTIALS OF  
SMALL ATOMIC CORES

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**Abstract:** Relativistic effective core potential (RECP) models for electronic structure calculations of atoms, molecules, clusters, and solids, satisfying the shape-consistence (norm conservation) requirement are presented and analyzed. To attain a high accuracy of predicting various physical properties with field-independent RECP models, both valence and subvalence (outer-core) electronic shells should be left for explicit treatment, so that only inner (“small”) electronic cores can be replaced by RECPs. Conventional semilocal shape-consistent RECPs are not uniquely defined in the small-core case, and none of the possible definitions seems to be ideal. The origin of limited accuracy of semilocal models is considered in some detail. Substantial improvements are achieved through the use of a more general Ansatz for RECP operators implying the action of different potentials on the outer core and valence shells.

## 1. INTRODUCTION

Effective core potential (ECP) or pseudopotential approach is an extremely popular tool for electronic structure calculations of molecular systems and solids comprising heavy-element atoms. The replacement of the all-electron problem by a simpler one restricted to a subsystem of “active” electrons reduces dramatically the computational cost of both *ab initio* methods and density functional theory (DFT). ECPs are particularly suitable for accurate and inexpensive treatment of large relativistic effects since the many-electron problem with relativistic ECP (RECPs) formally resembles that for non-relativistic systems and one can make use of efficient modern methods of non-relativistic quantum chemistry with minor modifications. The RECPs derived from the first principles are normally generated on the basis of accurate relativistic calculations of free atoms or / and atomic ions. Numerous Ansätze for RECP and various techniques to extract RECP parameters from all-electron data have been proposed (see Refs. [1, 2] for reviews). The most popular and numerically stable procedure of RECP construction

implies the fulfillment of the so-called “shape-consistency” requirement: atomic one-electron spinors obtained with RECP (pseudospinors) should fit the corresponding spinors from all-electron calculations outside of a spherical domain near the nucleus. Extensive databases on such shape-consistent RECPs (solid state physicists prefer the term “norm-conserving pseudopotentials”) are now readily available (see e.g. [3]). The optimum number of electrons left for explicit treatment is normally larger than that of “true” valence electrons since the neglect of core-valence correlations and core polarization can lead to significant errors. This is especially important for heaviest elements because the shell structure of heavy atoms is in a sense blurred by the strong relativistic contraction of *s* and  $p_{1/2}$  subshells along with a certain expansion of high angular momentum subshells. This effect is illustrated in Fig. 1 representing partial radial charge distributions associated with particular subshells in the group 12 elements. For a relatively light Zn atom, the spatial localizations of outer-core subshells  $3s$  and  $3d$  are quite similar, strongly differing from that for the outermost  $4s$  subshell. When the nuclear charge increases, the distribution associated with the (subvalence)  $(n - 1) d$  shell moves toward that for the valence  $ns$  subshell (Hg), so that for the superheavy element 112 (Cn) the differences between

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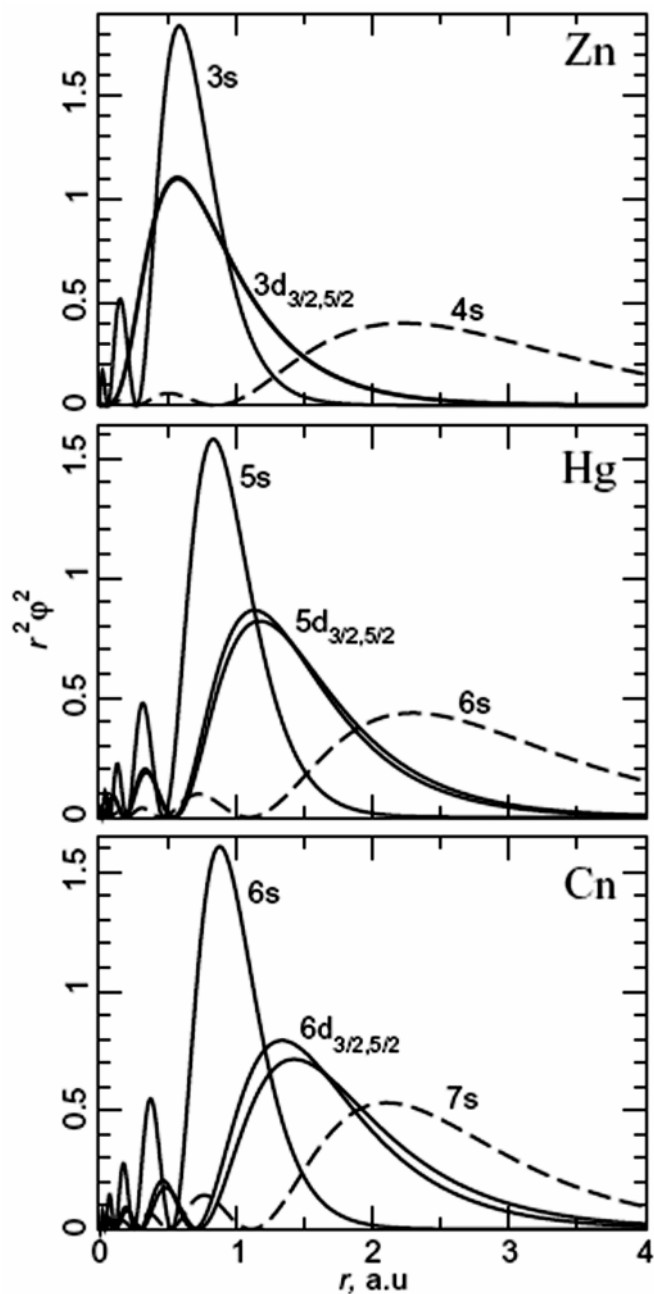
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the  $6s$  and  $6d$  distributions are comparable to the intershell ( $n = 6$ ) – ( $n = 7$ ) differences and the shell structure is hardly discernible. To attain a high accuracy in RECP-based calculations, it is thus necessary (but not sufficient) to consider explicitly the electrons associated with outer core (sometimes called semicore or subvalence) shells, eliminating only the most localized inner-core electrons. The corresponding RECPs are usually referred to as “small-core” ones, in contradistinction with “large-core” RECPs where the separation into active (valence) and core electrons generally agrees with the conventional viewpoint of chemists.

It should be noticed, however, that the procedure of shape-consistent RECP constructing is well defined only for the large-core model; its extension to the small-core case is not straightforward nor unique, encountering serious conceptual and practical problems. The solution of these problems is essential for converting the RECP approach which was generally considered earlier as a basis of economical intermediate-accuracy techniques of electronic structure calculations into a tool for highly accurate calculations on ground and electronically excited states of atoms, molecules and clusters. Quite recently it was shown that the use of somewhat sophisticated Ansätze for the small-core shape-consistent RECPs and the extraction of their parameters from high-level relativistic calculations on free atoms can ensure remarkable accuracy in predicting various properties of molecular and supramolecular systems and chemical reactions; errors arise mainly from approximations that should be necessarily introduced to solve the many-electron correlation problem rather than from the RECP model itself.

When choosing some particular RECP model for the calculations on systems containing heavy atoms, one should clarify whether the selected RECP provides the required level of accuracy in the considered domain of its application. At the same time limited computational facilities can impose certain restrictions on the acceptable complexity of RECP models. As a result, different types of RECPs are used for the studies on small molecules by wavefunction techniques and large polyatomic systems or solids by DFT methods. In the former case, the main requirement to an RECP is its high accuracy, while in the latter case the form of RECP operators should be first of all convenient for rapid and properly scaling calculations.



**Fig. 1:** Orbital contributions to radial electron densities ( $r^2\phi^2$ ) for the Zn, Hg and element 112 (Cn) atoms. Solid lines:  $n - 1$  (subvalence) shells, dashed lines:  $n$  (valence) shells

In the present review, we discuss the possible generalizations of the shape-consistent RECP concept to the “small-core” case. The restrictions imposed by the shape-consistency requirement on the solutions of SCF equations for the RECP model are analyzed in some details. The main ways to build these RECPs in the semi-local (radially-local) form are presented and compared; their shortcomings are avoided through introducing the concept of Generalized RECP (GRECP) which goes

beyond the semilocal Ansatz. The use of GRECP allows to dramatically improve the accuracy of electronic structure calculations, especially for excited electronic states.

## 2. RELATIVISTIC EFFECTIVE CORE POTENTIALS

Within the relativistic effective core potential approximation, the effective Hamiltonian for an atom is usually written in the form

$$\mathbf{H}^{\text{eff}} = \sum_{p_v} [\mathbf{h}(p_v) + \mathbf{U}(p_v)] + \sum_{p_v > q_v} \frac{1}{r_{p_v q_v}}. \quad \dots (1)$$

The summation in Eq. (1) runs over a subset of electrons, which are treated explicitly and marked by the indices  $p_v$  and  $q_v$ .

This subset comprises the electrons of valence and often outer core shells. Here  $r_{p_v q_v}$  denotes the distance between the  $p_v^{\text{th}}$  and  $q_v^{\text{th}}$  electrons,  $\mathbf{h}$  is the one-electron Schrödinger Hamiltonian:

$$\mathbf{h} = -\frac{1}{2}\Delta - \frac{Z_{ic}}{r}, \quad \dots (2)$$

where  $Z_{ic}$  is the nuclear charge minus the number of removed core electrons and  $r$  denotes the distance between the electron and the nucleus.  $\mathbf{U}$  is the RECP (or relativistic pseudopotential) operator. The extension of Eq. (1) to polyatomic system is straightforward provided that we assume that the RECP of the whole system is simply the linear superposition of atomic RECP operators.

The RECP operator simulates, in particular, interactions of the explicitly treated electrons with those which are excluded from the RECP calculations. Contrary to the four-component wavefunctions used in relativistic all-electron calculations, the wavefunctions in the RECP case (pseudo-wavefunctions) can be both one- and two-component; in the latter case we shall use the term ‘‘pseudospinors’’.

The RECP method is based on the ‘‘frozen core’’ approximation and it is clear that reducing the number of core electrons leads to an increase in the accuracy of this approximation.

Let us list the main advantages of the RECP approach:

- it allows one to exclude from the calculations a large number of inactive electrons and to treat explicitly only valence (and outercore) electrons from the beginning,
- pseudospinors are smooth in the core regions of heavy atoms and thus more suitable for analytic approximations and numerical treatment than oscillating true valence spinors.
- the small components of four-component spinors are eliminated and the nonrelativistic kinetic energy operator is used. Therefore the RECP approach allows one to use a well-developed nonrelativistic electronic structure methods with moderate modifications required to comply with the spin-dependence of the RECP operators accounting for the effects of relativity. Breit and other two-electron quantum electrodynamic (QED) interactions can be efficiently treated within the one-electron RECP model.
- Correlation molecular calculations with RECPs are naturally performed in the basis of spin-orbitals (and not of spinors as is in all-electron four-component calculations) even for the cases when QED effects are taken into account. This allows one to reduce dramatically the cost.

## 3. SEMILOCAL ANSÄTZ FOR THE RECP OPERATORS

The semilocal RECP Ansatz is widely used in the calculations on ground and excited electronic states of molecules with heavy elements. The RECP operator  $\mathbf{U}$  for an atom is usually written in the form:

$$\mathbf{U} = U_{LJ}(r) + \sum_{l=0}^L \sum_{j=|l-1/2|}^{l+1/2} [U_{lj}(r) - U_{LJ}(r)] \mathbf{P}_{lj} \quad \dots (3)$$

where  $U_{lj}(r)$  are conventional functions of the distance  $r$  from the nucleus,  $\mathbf{P}_{lj}$  denotes the projector onto the subspace of two-component spinors with the orbital and total angular momentum values  $l$  and  $j$  respectively,  $J = L + 1/2$ ,  $L = l_c^{\text{max}} + 1$  and  $l_c^{\text{max}}$  is the highest orbital momentum of the core spinors.

Using the identities for the  $\mathbf{P}_{lj}$  projectors [4],

$$\mathbf{P}_{l, j=l\pm 1/2} = \frac{1}{2l+1} \left[ \left( l + \frac{1}{2} \pm \frac{1}{2} \right) \mathbf{P}_l \pm 2\mathbf{P}_l \bar{\mathbf{l}} \cdot \bar{\mathbf{s}} \mathbf{P}_l \right], \dots (4)$$

where  $\mathbf{P}_l$  projects onto the subspace spanned by all spinors with the orbital momentum  $l$  and  $\bar{1}$  and  $\bar{s}$  are the operators of the orbital and spin momenta, the RECP operator can be rewritten in the “spin-orbit” representation:

$$\mathbf{U} = U_{LJ}(r) + \sum_{l=0}^L [\bar{U}_l(r) - U_{LJ}(r)] \mathbf{P}_l + \sum_{l=1}^L \frac{2}{2l+1} \Delta U_l(r) \mathbf{P}_l \bar{1} \cdot \bar{s} \mathbf{P}_l \quad \dots (5)$$

Here  $\bar{U}_l = (2l+1)^{-1} [(l+1)U_{l,j=l+1/2} + lU_{l,j=l-1/2}]$  are the components of spin-averaged RECP and  $\Delta U_l = U_{l,j=l+1/2} - U_{l,j=l-1/2}$ . The last sum in Eq. (5) is referred to as effective spin-orbit operator.

**Shape-consistent semilocal RECPs:** The shape-consistent RECP model implies the smoothing of valence spinors in the core regions. Consider the shape-consistent semi-local (or radially-local) RECP model developed by K. Pitzer’s group [5, 6]. The nodeless radial parts  $\phi_{n,lj}(r)$  of atomic pseudospinors  $\Phi_{n,lj}(r)$  are constructed of the radial parts  $f_{n,lj}(r)$  of large components of the valence ( $v$ ) Dirac–Fock spinors (one pseudospinor for each pair of orbital  $l$  and total  $j$  momentum quantum numbers) as:

$$\phi_{n,lj}(r) = \begin{cases} f_{n,lj}(r), & r \geq R_c, \\ a(r), & r < R_c, \end{cases} \quad \dots (6)$$

where  $r$  is the distance between the nucleus and electron. The matching (or core) radius,  $R_c$ , is chosen near the outermost extremum for the large component and  $a(r)$  is a smooth and nodeless function (usually a polinom) which tends to be proportional to  $r^\gamma$  near the nucleus. The power  $\gamma$  is typically chosen higher than  $l+1$  to ensure an efficient ejection of the valence electrons from the core region.

To derive the RECP components  $U_{lj}$ , the Hartree–Fock equations for valence pseudospinors (formally nonrelativistic but with  $j$ -dependent potentials) are inverted:

$$U_{lj}(r) = \phi_{n,lj}^{-1}(r) \left( \frac{1}{2} \frac{d^2}{dr^2} - \frac{l(l+1)}{2r^2} + \frac{Z_{ic}}{r} - \mathbf{J}(r) + \mathbf{K}(r) + \varepsilon_{n,lj} \right) \phi_{n,lj}(r), \quad \dots (7)$$

where  $\mathbf{J}$  and  $\mathbf{K}$  are the Coulomb and exchange operators. One-electron energies  $\varepsilon_{n,lj}$  are assumed to coincide with those for the original spinors.

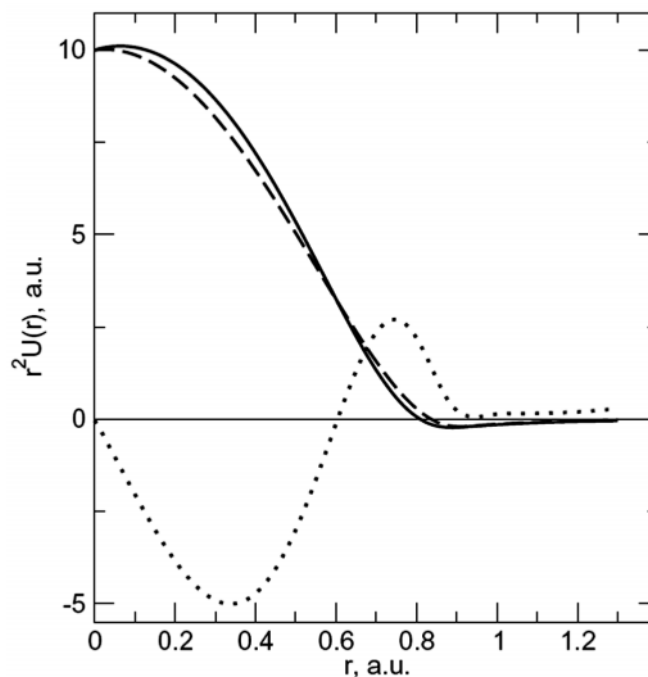
The success of the shape-consistent RECPs in describing electronic structure of many-electron systems (molecules, clusters and solids, including those containing very heavy atoms [7]) and different properties (chemical bonding, reactions, low-energy excitation spectra, transition probabilities, etc.) is not accidental; it is based on numerous ideas and developments done by several groups during decades (see [4–6, 8–13] and references). The final goal of those improvements was to increase “transferability” and accuracy of the RECP approximation in different applications, minimizing the computational cost of the electronic structure calculations. Nevertheless, one can reformulate the modern theory of the shape-consistent semi-local RECP on the basis of only two underlying natural propositions [14, 15] which are of crucial importance for the accuracy and transferability of RECPs: (a) proportionality of valence and low-energy virtual spinors and uniform scaling of partial-wave contributions to these spinors in the core region upon a perturbation localized in the valence region, (b) minimization of the “unphysical” RECP terms in the valence region; in other words, the simulated interactions of electrons in “pseudoatom” should match accurately enough the original ones in the valence region.

At present, different versions of semi-local RECPs with the same number of removed electrons provide a comparable level of accuracy. In principle, the addition of outer core electrons to the explicitly treated subsystem should improve the results. The decrease of  $R_c$  when the outercore pseudospinors get nodeless instead of the valence ones should lead to a better description of two-electron interactions. Nevertheless, as has been shown in all our calculations with semi-local RECPs, the extension of this subsystem beyond a certain limit does not lead to a further reduction of errors. Typical errors in dissociation and excitation energies for low-lying electronic states arising from the RECP approximation remain in the range up to 2000  $\text{cm}^{-1}$  and even more.

**“Core” and “valence” semilocal RECPs:** In the case of small-core RECP models both the valence and outercore subshells with the same  $lj$  quantum numbers are treated explicitly, and there is an ambiguity in choosing the spinors for which the potentials should be generated. One can avoid this ambiguity by extracting the RECP from the solutions for an appropriate ionic state of the atom [1], in which the outermost pseudospinors become nodeless. Obviously this stratagem can be reasonable only if the latter requirement can be fulfilled for an ionic state with rather small charge. As has been shown in Refs. [16, 17], the use of ionic configurations to generate small-core shape-consistent RECP is often not the best choice.

An alternative consists in generating the RECP components only for the outercore or valence pseudospinors using the correct reference atomic state with both outercore and valence spinors occupied. The generation of the “core” RECP through inverting the radial Hartree–Fock equations for outercore pseudospinors having no radial nodes is straightforward. In contrast, the valence pseudospinors in the small-core case normally do have such nodes. In this case, any attempts to directly invert the Hartree–Fock equations would yield singular potentials  $U_{lj}$  because the zeros of the denominator and numerator in Eq. 7, as a rule, do not coincide. However, in practice, these zeros are close to each other as was demonstrated in Ref. [18] and the most appropriate solution of this problem is to interpolate the potential in the vicinity of the pseudospinor node. The error in reproducing the one-electron energy due to such interpolation can be made small because the pseudospinors are small in the vicinity of the node. It does not exceed the errors arising from smoothing the spinors and the approximate treatment of the interaction with the inner core electrons [16]. Moreover, this trick should not affect the transferability of the resulting RECP since the node position is virtually unchanged upon the formation of chemical bonds and low-energy electronic excitations. The example in Fig. 2 shows that the resulting RECP which we shall call “valence” RECP can differ essentially from the “core” one. This difference can be partially explained by the following simple reasonings. The valence and outercore spinors with the same angular and total momenta behave differently in the vicinity of the last extremum of the outercore spinors (this stems from the orthogonality condition). As a consequence, these spinors cannot be smoothed (along with their second derivatives!) in the same manner and therefore,

notably different potentials are usually obtained. At the same time, original low-energy virtual and valence spinors have very similar (up to a factor) behaviour in the region where the smoothing is performed, and the potentials for all the smoothed virtual pseudospinors can be essentially the same as for the valence ones. It is worth noting that the smoothing in the core region also contributes to the difference between the valence and outercore potentials in the valence region [15].



**Fig. 2:** Potentials (multiplied by  $r^2$ ) for the outer core (5s) and valence (6s) pseudospinors of Hg (solid and dashed lines respectively) and their difference multiplied by 10 (dotted line)

Let us notice that there are several ways to circumvent the difficulties arising from the presence of radial nodes of valence pseudospinors in generating the potential components  $U_{lj}(r)$ . For instance, only the fitting of total valence energies for several atomic states (rather than the shapes of the pseudospinors in the valence region) is used to extract the parameters of the RECP by Stuttgart group (see [2] and references therein).

It is clear that the “core” RECP is non-optimal for describing the valence shells and therefore it is not the tool of choice for the modeling of chemical properties and low-energy electronic excitations. The “valence” RECP model is apparently more adequate (see Table 1). Unfortunately, the rough description of the outer core shell within the “valence” RECP approximation will also lead to non-negligible errors for valence electronic states because of

the inaccurate reproduction of screening of the nucleus. Therefore, the problem of choice between the “core” and “valence” semilocal RECPs appears. This problem is correctly eliminated in the Generalized RECP version. It allows one to attain practically any desired accuracy.

#### 4. GENERALIZED RECP

The GRECP concept was introduced and developed in a series of papers (see Refs. [14, 19–22] and references). The GRECP Ansatz is very flexible and covers semilocal, separable and Huzinaga-type [23] Ansätze for RECPs. Additionally, the GRECP operator can include terms of other types, e.g. “self-consistent” and two-electron “term-splitting” corrections [14, 19, 24], which are important first of all for economical but accurate treatment of transition metals, lanthanides and actinides. With these terms, the accuracy provided by GRECPs can be even higher than that of the frozen core approximation with the same number of explicitly treated electrons, accounting for the relaxation of removed inner core shells [14]. In this review we shall restrict our attention to rather simple field-independent one-electron form of GRECPs.

In contrast to other RECP methods, GRECP perfectly fits to the idea of separating the atomic shell into three groups: inner core, outer core and valence, which are treated differently. The scheme employed to generate the GRECPs naturally extends that for the semilocal shape-consistent RECP (see Section 3). In the most common case of no more than one outer-core spinor for each  $lj$  pair, the GRECP operator  $\mathbf{U}_G$  can be written in the following form:

$$\mathbf{U}_G = \mathbf{U}_v + (\mathbf{U}_c - \mathbf{U}_v) \mathbf{P}_c + \mathbf{P}_c (\mathbf{U}_c - \mathbf{U}_v) - \mathbf{P}_c (\mathbf{U}_c - \mathbf{U}_v) \mathbf{P}_c \quad \dots (8)$$

where  $\mathbf{U}_c$  and  $\mathbf{U}_v$  are the “core” and “valence” semi-local RECPs respectively and  $\mathbf{P}_c$  is the projector on the subspace spanned by all outer core pseudospinors. The general expression for the GRECP operator can be found in Ref. [14]. One readily verifies that for any outer-core spinor  $\varphi_{n,ljm}$  ( $m$  stands for the projection of the total angular momentum)  $\mathbf{U}_G \varphi_{n,ljm} = \mathbf{U}_c \varphi_{n,ljm}$ . For any function from the valence subspace  $\varphi_{n,ljm}$  one gets:

$$\mathbf{U}_G \varphi_{n,ljm} = \mathbf{U}_v \varphi_{n,ljm} + \mathbf{P}_c (\mathbf{U}_c - \mathbf{U}_v) \varphi_{n,ljm} \quad \dots (9)$$

Taking into account Eq. (7) used to generate  $\mathbf{U}_v$ , one can demonstrate that for any outer-core pseudospinor  $\varphi_{n,ljm}$  and any valence one:

$$\langle \varphi_{n,ljm} | \mathbf{U}_c - \mathbf{U}_v | \varphi_{n,ljm} \rangle = 0$$

so that the second term in the r.h.s. of Eq. (9) vanishes and  $\mathbf{U}_G \varphi_{n,ljm} = \mathbf{U}_v \varphi_{n,ljm}$ . To summarize,  $\mathbf{U}_G$  combines “outer-core” and “valence” RECP, acting on outer-core and valence spinors as  $\mathbf{U}_c$  and  $\mathbf{U}_v$  respectively. The problem of choice between  $\mathbf{U}_c$  and  $\mathbf{U}_v$  is thus eliminated.

Let us notice that the last term in the r.h.s. of Eq. (8) act only within the finite-dimensional space of outer-core pseudospinors. One can check that the second and the third terms cancel any spinor orthogonal to two finite-dimensional sets, that of outer core functions  $\{ \varphi_{n,ljm} \}$  and the set of functions  $\{ (\mathbf{U}_c - \mathbf{U}_v) \varphi_{n,ljm} \}$ , and cannot produce anything orthogonal to these two sets, so that their action is restricted to finite-dimensional space spanned by these two set. In other words, all these terms are separable and the GRECP operator  $\mathbf{U}_G$  is the sum of the “valence” semi-local operator and a separable correction. This correction accounts for the difference between potentials for outer-core and valence shells. As has been shown in Ref. [25], this difference within the sphere  $r > R_c$  arises from the smoothing and often cannot be neglected without loosing the “chemical accuracy” of valence energies. A more detailed description of distinctive features of the GRECP as compared to the original RECP schemes is given in Refs. [16, 17, 26, 27]. Some other GRECP versions are described and discussed in details in Refs. [14, 19–22].

The spin-orbit representation of GRECPs similar to (5) which can be found in Ref. [17] is more suitable in practical applications to molecular calculations. Despite the relative complexity of the GRECP operator, the calculation of its one-electron integrals is not notably more expensive than that for the case of the conventional radially-local RECP operator.

#### 5. EXAMPLE: APPLICATION TO Hg AND HgH

Below we compare the accuracy of various RECP approximations in the calculations on the Hg atom and HgH molecule. The numerical self-consistent-field atomic calculations of excitation energies within the  $jj$ -coupling scheme allow one to test a quality of the different RECP versions avoiding the errors due to the basis set incompleteness. The deviations of the RECP excitation energies from those of all-electron Dirac–Fock calculations are presented in Table 1.

**Table 1**  
**Transition energies (cm<sup>-1</sup>) for Hg averaged over nonrelativistic configurations from the numerical SCF calculations with different RECP versions as compared with those from all-electron (AE) calculations**

Configuration	Transition Energy (AE)	Absolute Error				
		Ionic RECP		"Core" "Valence"		GRECP
		Ross et al. <sup>a</sup>	Tupitsyn et al. <sup>b</sup>	RECP	RECP	
5d <sup>10</sup> 6s <sup>2</sup>	0	0	0	0	0	0
5d <sup>10</sup> 6s <sup>1</sup> 6p <sup>1</sup>	35743	214	130	-304	-45	2
5d <sup>10</sup> 6s <sup>1</sup> 6d <sup>1</sup>	56932	219	102	-513	-47	3
5d <sup>10</sup> 6s <sup>1</sup> 5f <sup>1</sup>	62127	218	100	-511	-46	3
5d <sup>10</sup> 6s <sup>1</sup>	68990	218	100	-511	-46	3
5d <sup>10</sup> 6p <sup>1</sup>	122315	527	315	-762	-67	33
5d <sup>10</sup> 6d <sup>1</sup>	163282	608	323	-1094	-88	26
5d <sup>10</sup> 5f <sup>1</sup>	179712	612	319	-1089	-89	19
5d <sup>10</sup>	207331	612	319	-1081	-81	27
5d <sup>9</sup> 6s <sup>2</sup> 6p <sup>1</sup>	73391	142	250	672	447	411
5d <sup>9</sup> 6s <sup>2</sup>	113133	139	209	434	468	432
5d <sup>9</sup> 6s <sup>1</sup> 6p <sup>1</sup>	163992	435	428	216	426	437
5d <sup>9</sup> 6s <sup>1</sup>	257802	522	428	-110	440	454
5d <sup>9</sup> 6p <sup>1</sup>	325218	917	744	-255	439	503

<sup>a</sup>RECP from Ref. [30].

<sup>b</sup>RECP from Ref. [16].

The data in the table are divided into the groups according to the occupation number of the 5d shell. The use of the Generalized RECPs dramatically improve energy estimates for the transitions with constant 5d occupancies in comparison with all semi-local RECP versions. Excitations involving 5d electrons lead to rather significant relaxation effects, and all variants of RECP calculations treating the 5d shell as an outer-core one cannot accurately reproduce the energies for the corresponding transitions. Systematic errors of the GRECP model (ca. 400 cm<sup>-1</sup>) in this case can be eliminated, for instance, by incorporating "self-consistent" terms in the RECP operator [24] or via explicit treatment of the next outer-core (4d) shell. A detailed analysis of errors concerning the excitations from outer-core shells is given in Ref. [14].

Much more reliable transition energy estimates accurately accounting for electron correlations are obtained by the Fock-space Relativistic Coupled Cluster

(RCC) method (see the review [28] and references therein). RECP errors in reproducing the all-electron RCC transition energies in Hg for the case of 20 correlated electrons and equivalent correlation [7, 9, 8, 6, 7, 7] basis sets for all-electron and RECP calculations [29] are presented in Table 2. The largest absolute errors in reproducing the transition energies with single-electron excitation or ionization are 94 cm<sup>-1</sup> for the GRECP [16] and 729 cm<sup>-1</sup> for the semi-local RECP of Ross et al. [30]. The same number of electrons, twenty, is explicitly treated in all these RECP versions. The larger errors for the RECP [30] are mainly due to the neglect of the difference between the outer core and valence potentials in semi-local RECP versions (see [14, 16] for more details).

**Table 2**  
**RCC transition energy estimates (cm<sup>-1</sup>) for Hg with different RECP versions as compared with those from all-electron RCC calculations**

State (leading configuration, term)	Transition energies	Errors <sup>c</sup>	
		All-el. DC	20 el. RECP of Ross et al. <sup>b</sup>
5d <sup>10</sup> 6s <sup>2</sup> (1S <sub>0</sub> ) →			
5d <sup>10</sup> 6s <sup>1</sup> 6p <sup>1</sup> (3P <sub>0</sub> )	37260	-10	363
5d <sup>10</sup> 6s <sup>1</sup> 6p <sup>1</sup> (3P <sub>1</sub> )	39091	4	378
5d <sup>10</sup> 6s <sup>1</sup> 6p <sup>1</sup> (3P <sub>2</sub> )	43925	28	437
5d <sup>10</sup> 6s <sup>1</sup> 6p <sup>1</sup> (1P <sub>1</sub> )	55095	79	416
5d <sup>10</sup> 6s <sup>1</sup> (2S <sub>1/2</sub> )	84215	36	482
5d <sup>10</sup> 6s <sup>1</sup> (2S <sub>1/2</sub> ) →			
5d <sup>10</sup> 6p <sup>1</sup> (2P <sub>1/2</sub> )	51734	-9	428
5d <sup>10</sup> 6p <sup>1</sup> (2P <sub>3/2</sub> )	60883	11	539
5d <sup>10</sup> (1S <sub>0</sub> )	150720	-58	729

<sup>a</sup>The GRECP from reference [16].

<sup>b</sup>The RECP from reference [30].

<sup>c</sup>In this table, errors were calculated as differences between the transition energies from the RECP and all-electron calculations for the same number of correlated electrons and equivalent basis sets.

The calculated parameters for the ground states of HgH and HgH<sup>+</sup> are collected in Table 3. Two series of GRECP/RCC calculations with single, double, and estimated triple amplitudes, SDT, were performed. In the first series, the ground state of the HgH<sup>+</sup> ion served as reference (denoted RCC-1, and the Fock-space scheme was



**Table 3**  
Spectroscopic constants of the ground states of the HgH molecule and HgH<sup>+</sup> Ion.  $R_e$  is in Å,  $D_e$  in eV, other values in cm<sup>-1</sup>

	$R_e$	$\omega_e$	$D_e$	$B_e$	$\omega_e x_e$	$\alpha_e$
			HgH	$^2\Sigma_{1/2}^+$		
<b>Experiment</b>						
Ref. [36]	1.741	1385	0.46	5.55	75	0.271
Ref. [37]	1.740	1387	0.46	5.55	83	0.312
Ref. [38]	1.735	1421	0.46	5.59	121	0.404
<b>GRECP calculations [40]</b>						
RCC-1	1.730	1424	0.41	5.62	81	0.343
RCC-2	1.738	1362	0.41	5.56	93	0.380
<b>All-electron calculations [31]</b>						
RCC-1	1.753	1359	0.40	5.30	89	
RCC-2	1.758	1361	0.40	5.26	108	
			HgH <sup>+</sup>	$^1\Sigma_0^+$		
<b>Experiment</b>						
Ref. [39]	1.594	2028	(3.11) <sup>a</sup>	6.61	41	0.206
Ref. [37]	1.594	2034	(2.4) <sup>a</sup>	6.61	46	0.206
<b>GRECP Calculations [40]</b>						
RCC-1	1.591	2044	2.70	6.64	41	0.208
RCC-2	1.596	2051	2.59	6.60	32	0.185
<b>All-electron calculations [31]</b>						
RCC-1	1.607	2020	2.55	6.42	33	

<sup>a</sup>Cited in Refs. [37, 39] as uncertain.

with electrons added in the lowest unoccupied  $\sigma$  and  $\pi$  orbitals of HgH<sup>+</sup>. The second series (RCC-2) started from the ground state of the HgH<sup>-</sup> ion as reference, using the Fock-space scheme:



with electrons removed from the highest occupied  $\sigma$  orbital of HgH<sup>-</sup>. Spectroscopic constants of the HgH ground state are in excellent agreement with the experimental data. The differences between the results obtained with the two Fock-space schemes are small. Such differences arise from the truncation of the cluster

operator, and indicate omitted contributions from higher excitations. Similar behavior is observed the ground state of HgH<sup>+</sup>. Here, the results obtained with scheme (10) are slightly better than those of scheme (11) as might be expected; however the differences are still rather small. It should be noted that the results of the GRECP calculations performed with sufficiently large basis set should be compared with the experimental data rather than with that of all-electron Dirac-Coulomb (DC) calculations [31] because a relatively small basis set for Hg (in particular, without g-type functions) was used in the latter.

## 6. SEPARABLE PSEUDOPOTENTIALS

In calculations on large polyatomics and periodic systems, shape-consistent RECPs are usually approximated by separable operators (i.e. those acting within finite-dimensional subspaces). This stratagem dramatically reduces the computational work required to set up the RECP matrix in the cases when the valence/outer core many-electron problem is solved using delocalized (plane-wave) bases. If the basis is composed of localized functions, the corresponding savings are much less essential since the majority of integrals involving RECP can be neglected a priori due to the strongly localized nature of pseudopotential operators. Nevertheless, in this case separable RECPs still can be a tool of choice due to the simplicity and numerical stability of requisite computational algorithms.

A straightforward separable approximation to the RECP  $\mathbf{U}$  is immediately obtained through defining a finite (normally one-center) set of one-electron functions  $\{\chi_p\}$  and projecting  $\mathbf{U}$  onto the subspace  $\mathcal{L}$  spanned by this set: [32]

$$\mathbf{U}_{sep} = \sum_{pq} |\chi_p\rangle (\mathbf{S}^{-1} \mathbf{U} \mathbf{S}^{-1})_{pq} \langle \chi_q|, \quad \dots (12)$$

where  $\mathbf{S}$  denotes the overlap matrix,  $\mathbf{S}_{pq} = \langle \chi_p | \chi_q \rangle$ , and  $\mathbf{U}$ :  $\mathbf{U}_{pq} = \langle \chi_p | \mathbf{U} | \chi_q \rangle$  is the RECP matrix. One should notice that (i) because of strong localization of  $\mathbf{U}$  in the core region, it is usually senseless to choose  $\{\chi_p\}$  as a one-center subset of the basis used to solve the valence / outer core many-electron problem, (ii) even for the functions from  $\mathcal{L}$  ( $\varphi \in \mathcal{L}$ ),  $\mathbf{U}_{sep} \varphi \neq \mathbf{U} \varphi$  unless  $\{\chi_p\}$  is complete since  $\mathbf{U}_{sep} \varphi$  is the projection of  $\mathbf{U} \varphi$  onto  $\mathcal{L}$ . It is not thus surprising that a reasonable accuracy implies the use of rather large subspaces  $\mathcal{L}$  comprising the



functions localized in the core region. For instance, a few dozens of primitive Gaussians should be included in  $\{\chi_p\}$  to avoid significant errors due to the approximation (12).

The abovementioned shortcomings are partially avoided through passing to an alternative separable approximation for  $\mathbf{U}$  [33–35] acting within the subspace spanned by the functions  $\{\mathbf{U}\chi_p\}$ , where  $\{\chi_p\}$  is still a pre-defined set of one-electron functions:

$$\mathbf{U}_{sep} = \sum_{pq} |\mathbf{U}\chi_p\rangle (\mathbf{U}^{-1})_{pq} \langle \mathbf{U}\chi_q|. \quad \dots (13)$$

It might be worth noting that the operator (13) does not exactly coincide with (but does not strongly differ from) the restriction of  $\mathbf{U}$  onto the subspace spanned by  $\{\mathbf{U}\chi_p\}$ . One readily verifies that now  $\mathbf{U}_{sep}\phi = \mathbf{U}\phi$  for any function  $\phi$  from  $\mathcal{L}$ . Due to this fact, the use of  $\mathbf{U}_{sep}$  (13) is very efficient at least in DFT calculations. Provided that the set  $\{\chi_p\}$  is composed of atomic pseudoorbitals, rather accurate DFT results are normally obtained with very small dimensions of  $\mathcal{L}$  (normally 3-5 for each pair of  $j, l$  values). A remarkable advantage of the operator (13) is that it is well-defined even for  $\{\chi_p\}$  having radial nodes; to determine it completely, it is sufficient to know the functions  $\{\chi_p\}$  and  $\{\mathbf{U}\chi_p\}$ . Formally, the potentials  $\mathbf{U}$  can be divergent at the nodes of the corresponding orbitals. Note that the separable correction added to the semi-local RECP to form the GRECP operator shares the main advantages of the  $\mathbf{U}_{sep}$  operator (13).

Unfortunately, one cannot consider the separable representation (13) as a panacea. Let us recall that the components of semilocal (or generalized)  $\mathbf{U}$  are usually repulsive. Since  $\mathbf{U}_{sep}$  (13) simply kills any function orthogonal to all  $\mathbf{U}\chi_p$ , the repulsive contribution from  $\mathbf{U}$  to the one-electron energy associated with such function will be lost, so that this energy will be too low. In the cases, when  $\mathcal{L}$  is spanned by a minimum set of atomic one-electron function, this lead to a collapse of solutions even at the DFT level (so-called “ghost state effect”) rapidly disappearing when excited atomic functions are added to  $\{\chi_p\}$ . The latter trick is not so useful in correlation wavefunction calculations. For instance, it does not efficiently eliminate the lowering of one-electron energies for “correlation” functions which are localized in the outer-core region but orthogonal to outer-core functions. Invoking the perturbation theory argumentation, one can easily realize that the corresponding

contributions to correlation energies will be overestimated.

It is often advantageous to build separable approximations for the non-local parts of RECP (e.g.  $U_{ij}(r) - U_{LJ}(r)$  in Eq. (3)) rather than for the whole RECP operators.

In practice, the separable operators (12) or (13) are usually reduced to sums of weighted projectors onto one-dimensional subspaces by an appropriate transformation  $\{\chi_p\} \rightarrow \{\tilde{\chi}_p\}$  within  $\mathcal{L}$ , diagonalizing the matrices  $\mathbf{S}^{-1}\mathbf{U}\mathbf{S}^{-1}$  or  $\mathbf{U}$  respectively,

$$\mathbf{U}_{sep} = \sum_p |\tilde{\chi}_p\rangle u_p \langle \tilde{\chi}_p| \text{ or } \sum_p |\mathbf{U}\tilde{\chi}_p\rangle w_p \langle \tilde{\chi}_p\mathbf{U}|, \quad \dots (14)$$

where  $u_p$  or  $w_p$  are numerical amplitudes.

Separable approximations can be constructed for any type of field-independent RECP, and the complexity of molecular or solid-state calculations formally does not depend on the complexity of the RECP Ansatz. Nevertheless, in some cases the peculiarities of original models can affect the efficiency of separabilization. For instance, the use of Eq. (13) in molecular calculations with analytical (e.g. Gaussian) bases implies simple analytical (preferably also Gaussian) fitting of the functions  $\{\mathbf{U}\chi_p\}$ . Taking into account the advantages of using smooth AO-like  $\{\chi_p\}$ , one can realize that the presence of irregularities in valence-adapted or generalized pseudopotentials should give rise to certain difficulties in this fitting.

## 7. CONCLUDING REMARKS

The relativistic shape-consistent effective core potential theory was developed to perform moderate-accuracy molecular electronic structure calculations with minimal computational cost. It is demonstrated meanwhile that the modern shape-consistent RECP formulations can ensure a pretty high accuracy of calculation for molecules including those comprising very heavy atoms, still using essentially nonrelativistic-type (though spin-dependent) Hamiltonians. Recently it has been justified that the one-electron RECP operator, in addition, can very efficiently treat the interelectronic relativistic interactions including Breit ones, QED effects as well as arbitrary finite nuclear models.

The latest improvements of the shape-consistent RECP theory offer the possibilities to increase the

accuracy of the shape-consistent effective potential model to a level yet inaccessible by the modern *ab initio* correlation methods and codes even for a few-atomic many-electron systems. It is also pointed out that the shape-consistent RECP theory with semi-local effective operators can be deduced from natural theoretical propositions. In turn, the further improvement of accuracy requires to employ more sophisticated small-core RECP operators taking into account some non-local (but separable) terms.

Being reformulated in the frameworks of computationally more efficient separable effective operators, the shape-consistent RECP approach is very suitable for calculations of large polyatomic and extended systems when the density functional theory is applied to take into account the effects of electron correlations.

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