Accounting for correlations with core electrons by means of the generalized relativistic effective core potentials: Atoms Hg and Pb and their compounds.

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A way to account for correlations between the chemically active (valence) and innermore (core) electrons in the framework of the generalized relativistic effective core potential (GRECP) method is suggested. The “correlated” GRECP’s (CGRECP’s) are generated for the Hg and Pb atoms. Only correlations for the external twelve and four electrons of them, correspondingly, should be treated explicitly in the subsequent calculations with these CGRECP’s whereas the innermore electrons are excluded from the calculations. Results of atomic calculations with the correlated and earlier GRECP versions are compared with the corresponding all-electron Dirac-Coulomb values. Calculations with the above GRECP’s and CGRECP’s are also carried out for the lowest-lying states of the HgH molecule and its cation and for the ground state of the PbO molecule as compared to earlier calculations and experimental data. The accuracy for the vibrational frequencies is increased up to an order of magnitude and the errors for the bond lengths (rotational constants) are decreased in about two times when the correlated GRECP’s are applied instead of earlier GRECP versions employing the same innercore-outercore-valence partitioning.

I. INTRODUCTION.

Accurate calculations of electronic structure of molecules are required in various fields of both basic research and practical applications. To attain high accuracy, correlations not only for chemically active (valence and sometimes outermost core) but also for innermore electrons often have to be taken into account. The number of the latters can be rather large (see atomic calculations below). For brevity, we will further refer in introduction to these external chemically active and innermore core electrons as just to the “valence” and “core” ones, correspondingly.

It was studied, e.g., in papers\textsuperscript{1,2} for the Hg and Pb atoms that neglecting the correlations between the valence and core electrons leads to significant errors in calculating transition energies already between lowest-lying states. The 5p and innermore shells of Hg as well as the 5d and innermore shells of Pb were considered as the core shells in Refs.\textsuperscript{1,2} whereas the outermore shells were treated as valence. The correlations between the core and valence electrons which also include the terms of “core-...-core-valence”-type in high orders of perturbation theory are called below as core correlations. We will further consider only such a part of the core correlations which can be taken into account in a relativistic calculation of a free atom with the codes fully exploiting spherical symmetry. The problem is that the computational efforts very fast grow with increasing the number of correlated electrons if the two-electron interactions are treated explicitly. Therefore, the approximate methods which allow one to treat the core correlations by a simplified way are of considerable practical interest for accurate calculations. It is, obviously, reasonable to account for the core correlations already at the stage of constructing effective atomic Hamiltonians if the separation of atomic shells on the valence and core spaces is done appropriately (by analogy with the procedure of freezing atomic core shells in molecular calculations, see section\textsuperscript{1,13}). The question under consideration in the paper is concerning the accuracy of the large-core one-electron relativistic effective core potentials (RECP’S) in simulating the energy-dependent effects of correlations between atomic core and valence electrons in heavy-atom molecules which include in general also two-electron and higher order core-valence interactions.

The RECP method is widely used for calculations of molecules containing heavy atoms\textsuperscript{3} because it reduces drastically the computational cost as compared to the all-electron four-component approach both at the integral generation–transformation stages and at the stage of correlation calculation when the spin-orbit basis set and two-step schemes of accounting for spin-orbit interaction etc. are used. It is demonstrated both theoretically and computationally in Refs.\textsuperscript{1,2,4,5,6,7} that the RECP method can be used as a very accurate approximation not only for SCF calculations but for correlated calculations as well. In a series of papers\textsuperscript{4,7,8,9,10,11,12}, it is suggested to split a correlation calculation of a molecule containing heavy atoms onto computationally tractable consequent calculations in the valence and core regions, i.e. molecular RECP calculation at the first step and one-center restoration of electronic structure in atomic cores at the second step. In the two-step calculation, the computational efforts in correlating core and valence electrons will be roughly summed, whereas they have polynomial dependence on the number of explicitly treated electrons and on the basis set size in the one-step calculation since the number of varied parameters in correlation calculations (the numbers of coefficients in the configuration interaction or cluster amplitudes in the coupled cluster studies) grows proportionally to the number of the excitation operators used within a considered level of correlation treatment. In the present paper, a method of treatment of the core correlations with the help of the generalized
Hamiltonian \( (1) \) is written only for a valence subspace of electrons, which are treated explicitly and denoted by indices \( i_v \). The simulations are explicitly considered. When generating MC DF-SCPP operator can be presented in the form of the RECP (SCPP) approximation are discussed in the next section.

It should be noted that the present CGRECP’s and the core polarization potentials (CPP’s) suggested in Refs. simulate polarization-correlation effects by different ways. The CPP’s account directly for a displacement of core (dipole polarization) and radially asymmetric deformation of core (quadruple polarization etc.) due to the electrostatic forces acting on the core from the valence electrons, other cores, and external electric fields. However, they do not account accurately for the Pauli exclusion principle (requirement of orthogonality of electronic states in core to occupied states of valence electrons and to core states of neighboring atoms) that leads to neglecting spin-polarization of core etc. Moreover, the CPP’s do not take into account the effects of spherically symmetric relaxation of core due to the above described “core correlations”. In turn, the present CGRECP’s describe interactions between the spherically symmetric model of the correlated core and other electrons and nuclei. These interactions, in particular, account for the core correlations and some “spherically-averaged” polarization effects. (In more details, the one-electron part of the CPP operator accounts well for some part of the valence-core interactions (“vacuum polarization”-type terms) discussed above whereas its two-electron part accounts first of all for the valence-core-valence interactions (often called by “screening”-type terms). The latter are not perfectly approximated within the present CGRECP’s. In turn, the one-electron CGRECP’s account for the high-order correlation effects within the core itself which are not described by CPP’s.)

Sufficiently accurate correlation method is required to describe the core correlations in \( \text{ab initio} \) all-electron calculation, which are approximated then by the CGRECP (as one can conclude, e.g., from calculations of the Hg and Pb atom). One can see from Tables III and IV of the present paper that about one-half of the difference between the bond lengths calculated in the “frozen core” approximation and the experimental data can be described by the spherically-symmetric core correlation-relaxation. The incorporation of the GRECP and CPP methods to treat all the most important core correlation-relaxation (including polarization) effects simultaneously is suggested by us in future.

In Ref. only core polarization effects including mainly spin-orbit polarization and other “electrostatic polarization effects on the core arising from single excitations out of the \( (n-1) \) sub-valence shell” were taken into account by means of their multiconfigurational Dirac-Fock shape-consistent pseudopotentials (MCDF-SCPP’s). The spin-orbit polarization is automatically taken into account in our (and many other groups’) RECP’s because we generate two-component (spin-dependent) GRECP’s on the base of all-electron reference calculations with the Dirac-Coulomb-Breit Hamiltonian. Unlike Ref. the present CGRECP’s account for the core correlations. In order to account for the latter by means of an \( \text{ab initio} \) RECP, some reference \text{ab initio} calculation should be performed in which the simulated correlations are explicitly considered. When generating MCDF-SCPP’s, only one single \( (n-1)p \rightarrow (n+1)p \) excitation from the main configuration is used in the reference all-electron calculations. The polarization effects can be described in the all-electron calculation with the help of single excitations only but at least double excitations are necessary to describe correlations satisfactorily. Another question is concerning the possibility of the radially-local SCPP operator to reproduce the frozen core approximation with a good enough accuracy because the errors of the former can be, in principle, higher than the contribution of the core correlation-polarization effects. The forms of the operators should adequately describe the types of the described contributions whereas the errors of the radially-local SCPP approximation can not be properly compensated, e.g., by the CPP-type operator. The ways to increase accuracy of the RECP (SCPP) approximation are discussed in the next section.

II. GRECP METHOD.

When core electrons of a heavy-atom molecule do not play an active role, the effective Hamiltonian with RECP can be presented in the form

\[
\mathbf{H}^\text{ Ef} = \sum_{i_v} \left[ \mathbf{h}^{\text{Schr}}(i_v) + \mathbf{U}^\text{ Ef}(i_v) \right] + \sum_{i_v > j_v} \frac{1}{\tau_{i_v j_v}} .
\]

Hamiltonian \( \mathbf{H}^\text{ Ef} \) is written only for a valence subspace of electrons, which are treated explicitly and denoted by indices \( i_v \) and \( j_v \). In practice, this subspace is often extended by inclusion of some outer core shells for better accuracy. \( \mathbf{U}^\text{ Ef} \)
is an RECP (or relativistic pseudopotential) operator that can be written in the separable (e.g., see Ref. 19 and references) or radially-local (semi-local) approximations when the valence pseudospinors are smoothed in heavy-atom cores. Besides, the generalized RECP operator described below can be used that includes the radially-local, separable and Huzinaga-type relativistic pseudopotentials as its components and some special cases. Additionally, the GRECP operator can include terms of other types, called by "self-consistent" and two-electron "term-splitting" corrections, which are important first of all for most economical (but precise) treatment of transition metals, lanthanides and actinides. With these terms, accuracy provided by GRECP's can be even higher than the accuracy of the "frozen core" approximation (employing the same number of explicitly treated electrons) because they can account for relaxation of explicitly excluded (inner core) shells. In Eq. (1), $h^{\text{Schr}}$ is the one-electron Schrödinger Hamiltonian

$$h^{\text{Schr}} = -\frac{1}{2} \nabla^2 - \frac{Z_{ic}}{r},$$

where $Z_{ic}$ is the charge of the nucleus decreased by the number of inner core electrons. The (G)RECP operator simulates, in particular, interactions of the explicitly treated electrons with those which are excluded from the (G)RECP calculations. Contrary to the four-component wave function used in Dirac-Coulomb(-Breit) calculations, the pseudowave function in the (G)RECP case can be both two- and one-component. The use of the effective Hamiltonian instead of the all-electron relativistic Hamiltonians raises a question about its accuracy. It was shown both theoretically and in many calculations (see Ref. 4 and references) that a typical accuracy of the radially-local RECP versions is within 1000–3000 cm$^{-1}$ for transition energies between low-lying states.

The GRECP concept was introduced and developed in a series of papers (see Refs. 4,13,22,23,24 and references). In contrast to other RECP methods, GRECP employs the idea of separating the space around a heavy atom into three regions: inner core, outer core and valence, which are treated differently. It allows one to attain practically any desired accuracy, while requiring moderate computational efforts since the overall accuracy is limited in practice by possibilities of correlation methods.

### A. Generation of GRECP’s with the separable correction.

The main steps of the scheme of generating the GRECP version with the separable correction taken into account are:

1. The numerical all-electron relativistic calculation of a generator state is carried out for an atom under consideration. For this purpose, we use the HFDB code for atomic calculations by Dirac-Fock (DF) method (that can account also for the Breit effects self-consistently).

2. The numerical pseudospinors $\tilde{f}_{nlj}(r)$ are constructed of the large components $f_{nlj}(r)$ of the outer core and valence DF bispinors so that the innermost pseudospinors of them (for each $l$ and $j$) are nodeless, the next pseudospinors have one node, and so forth. These pseudospinors satisfy the following conditions:

$$\tilde{f}_{nlj}(r) = \begin{cases} f_{nlj}(r), & r \geq R_c, \\ y(r) = r^\gamma \sum_{i=0}^5 a_i r^i, & r < R_c, \end{cases}$$

where $n_v, n_c, n_{c'}$ are principal quantum numbers of the valence and outer core spinors, $L$ is one more than the highest orbital angular momentum of the inner core spinors. The leading power $\gamma$ in the polynomial is typically chosen to be close to $L+1$ in order to ensure sufficient ejection of the valence and outer core electrons from the inner core region. The $a_i$ coefficients are determined by the following requirements:

- $\{\tilde{f}_{nlj}\}$ set is orthonormalized,
- $y$ and its first four derivatives match $f_{nlj}$ and its derivatives at $R_c$,
- $y$ is a smooth and nodeless function, and
- $\tilde{f}_{nlj}$ ensures a sufficiently smooth shape of the corresponding potential.
$R_c$ is chosen near the extremum of the large component of the bispinor so that the corresponding pseudospinors have the defined above number of nodes. In practice, the $R_c$ radii for the different spinors should be chosen close to each other to generate smooth potentials.

3. The $U_{nlj}$ potentials are derived for each $l=0,\ldots, L$ and $j=\lfloor l+1/2 \rfloor$ for the valence and outer core pseudospinors so that the $\tilde{f}_{nlj}$ are solutions of the nonrelativistic-type Hartree-Fock equations in the jj-coupling scheme for a “pseudoatom” with the removed inner core electrons.

$$U_{nlj}(r) = \tilde{f}_{nlj}^{-1}(r) \left[ \frac{1}{2} \frac{d^2}{dr^2} - \frac{l(l+1)}{2r^2} + \frac{Z_{ic}}{r} - \tilde{J}(r) + \tilde{K}(r) + \varepsilon_{nlj} \right] \tilde{f}_{nlj}(r) + \sum_{n' \neq n} \tilde{\varepsilon}_{n'nlj} \tilde{f}_{n'lj}(r),$$

(4)

where $\tilde{J}$ and $\tilde{K}$ are the Coulomb and exchange operators calculated with the $\tilde{f}_{nlj}$ pseudospinors, $\varepsilon_{nlj}$ are the one-electron energies of the corresponding bispinors, and $\tilde{\varepsilon}_{n'nlj}$ are off-diagonal Lagrange multipliers (which are, in general, slightly different for the cases of the original bispinors and pseudospinors).

In the case of the pseudospinor with nodes, the potential is singular because the zeros of the denominator and numerator, as a rule, do not coincide. However, in practice, these zeros are close to each other as was demonstrated in Ref. 29 and in many cases this difference can not be neglected for “chemical accuracy” of valence energies. The more circumstantial description of this problem is interpolation of the potential in a vicinity of the pseudospinor node. The error of reproducing the one-electron energy due to such interpolation can be made small enough (because the pseudospinors are small in a vicinity of the node and the node position is not virtually changed at bond making and low-lying excitations). It does not exceed the errors of the GRECP approximation caused by smoothing the valence and outercore spinors and the approximate treating the interaction with the inner core electrons.

4. The GRECP operator in the separable correction written in the spinor representation is as

$$U_{\text{GRECP}} = U_{n_{L}nlj}(r) + \sum_{l=0}^{L} \sum_{j=\lfloor l+1/2 \rfloor}^{l+1/2} \left[ U_{n_{L}lj}(r) - U_{n_{L}lj}(r) \right] P_{lj} + \sum_{n_{c}} \left[ U_{n_{c}lj}(r) - U_{n_{c}lj}(r) \right] \tilde{P}_{n_{c}lj} + \sum_{n_{c},n_{c'}} \left[ U_{n_{c}lj}(r) - U_{n_{l}lj}(r) \right] P_{n_{c}lj}$$

(5)

where

$$P_{lj} = \sum_{m=-j}^{j} |ljm\rangle \langle ljm|, \quad \tilde{P}_{n_{c}lj} = \sum_{m=-j}^{j} |n_{c}ljm\rangle \langle n_{c}ljm|.$$  

$|ljm\rangle \langle ljm|$ is the projector on the two-component spin-angular function $\chi_{ljm}$, $|n_{c}ljm\rangle \langle n_{c}ljm|$ is the projector on the outer core pseudospinors $\tilde{f}_{n_{c}lj} \chi_{ljm}$, and $J = L + 1/2$.

5. The numerical potentials and pseudospinors can be fitted by gaussian functions to be used in calculations of polyatomic systems.

Two of the major features of the GRECP version with the separable correction described here are generating of the effective potential components for the pseudospinors which may have nodes, and addition of non-local separable terms with projectors on the outer core pseudospinors (the second and third lines in Eq. (5)) to the standard semi-local RECP operator (the first line in Eq. (5)). These terms account for difference between potentials for outercore and valence shells, which in $r > R_c$ is defined by smoothing within $R_c$ as is shown in Ref. 28 and in many cases this difference can not be neglected for “chemical accuracy” of valence energies. The more circumstantial description of distinctive features of the GRECP as compared to the original RECP schemes is given in Refs. 30-31. Some other GRECP versions are described and discussed in details in Refs. 24-28.

The GRECP operator in the spinor representation is naturally used in atomic calculations. The spin-orbit representation of this operator which can be found in Ref. 24 is more efficient in practice being applied to calculation of molecules. Despite the complexity of expression for 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.
B. Freezing the innermost shells from the outer core space.

It was noted in Refs. 27,32 that using essentially different matching radii \( R_x \) in Eq. 39 for different \( lj \) is not expedient since the (G)RECP errors are mainly set by the outermost from them (see below). In turn, explicit treatment of all of the outer core shells of an atom with the same principal quantum number is not usually reasonable in molecular (G)RECP calculations because of essential increase in computational efforts without serious improvement of accuracy. A natural way out is to freeze the innermost of them before performing molecular calculation but this can not be done directly if the spin-orbit molecular basis set is used whereas the core shells should be better frozen as spinors. In order to exclude (“freeze”) explicitly those innermost shells (denoted by indices \( f \) below) from molecular (G)RECP calculation without changing the radial node structure of other (outermore core and valence) shells in the core region, the energy level shift technique can be applied to overcome the above contradiction. Following Huzinaga et al., one should add the effective core operator \( U_{\text{Huz}}^{\text{eff}} \) containing the Hartree-Fock field operators, the Coulomb \( \mathbf{J} \) and spin-dependent exchange \( \mathbf{K} \) terms, over these core spinors together with the level shift terms to the one-electron part of the Hamiltonian:

\[
U_{\text{Huz}}^{\text{eff}} = (\mathbf{J} - \mathbf{K})[\tilde{f}_{n,lj}] + \sum_{n_j,l_j} B_{n_j,l_j} [\tilde{f}_{n_j,l_j}]\langle \tilde{f}_{n_j,l_j} \rangle \quad (\text{i.e.} \quad \varepsilon_{n_j,l_j} \rightarrow \varepsilon_{n_j,l_j} + B_{n_j,l_j}) ,
\]

where the \( B_{n_j,l_j} \) parameters are of order \( M|\varepsilon_{n_j,l_j}| \) and \( M > 1 \) (usually \( M \gg 1 \) in our calculations). Such nonlocal terms are needed in order to prevent collapse of the valence electrons to the frozen core states. They introduce some “soft orthogonality constraint” between the “frozen” and outermore electronic states.

All the terms with the frozen core spinors (the level shift operator and exchange interactions) can be transformed to the spin-orbit representation in addition to the spin-independent Coulomb term, using the identities for the \( \mathbf{P}_{lj} \) projectors:

\[
P_{lj=l\pm l/2} = \frac{1}{2l+1} \left[ \left( l + \frac{1}{2} \pm \frac{1}{2} \right) \mathbf{P}_l \pm 2\mathbf{P}_l \mathbf{I} \mathbf{s} \mathbf{P}_l \right] , \quad \mathbf{P}_l = \sum_{m_l=-l}^{l} |lm_l\rangle\langle lm_l| .
\]

where \( \mathbf{I} \) and \( \mathbf{s} \) are operators of the orbital and spin momenta, \( |lm_l\rangle\langle lm_l| \) is the projector on the spherical function \( Y_{lm_l} \).

More importantly, these outer core pseudospinors can be frozen in calculations with the spin-orbit basis sets and they can already be frozen at the stage of calculation of the one-electron matrix elements of the Hamiltonian, as implemented in the MOLGEP code. Thus, any integrals with indices of the frozen spinors are completely excluded after the integral calculation step. The multiplier \( M = 30 \) was chosen in the present molecular calculations to prevent mixing the shifted core states to the wavefunction due to correlations but not to get poor reference wavefunction in the initial spin-averaged calculations at the same time (as would be for \( M \rightarrow \infty \)).

The “freezing” of innermost shells from the outer core space within the “small core” GRECP’s is sometimes required because the accuracy of the GRECP’s generated directly for a given number of explicitly treated electrons cannot always correspond to the accuracy of the conventional frozen core approximation with the same space of explicitly treated electrons (without accounting for the frozen states). That space is usually chosen as a minimal one required for attaining a given accuracy. In fact, the “combined” GRECP, with separable and Huzinaga-type terms, is a new GRECP version treating the above number of electrons explicitly but which already provide the accuracy approaching to that of the frozen core approximation. The efficiency of using the “freezing” procedure within the GRECP method was first demonstrated in calculations\(^{16,33}\) of TI and TIH.

Let us consider the advantages of using the combined GRECP version as compared to the conventional RECP’s in reproducing the original core-valence interactions (correlation) on example of the Hg atom in more details. It is clear, that at least the 5d shell of Hg should be explicitly treated in accurate calculations of molecules containing Hg (e.g., see Ref. 3). For those calculations it would be optimal to use the RECP’s with 12 electrons of Hg treated explicitly (12e-RECP’s) such as the RECP of Ross et al. or our valence RECP version\(^{36}\). However, the explicit correlation of the outer core and valence electrons, occupying the 5d and ns, np, nd \((n = 6, 7, \ldots)\) orbitals, respectively, cannot be satisfactorily described in the framework of 12e-RECP’s with nodeless 5d, 6s and 6p pseudospinors, mainly because the smoothed valence pseudospinors have the wrong behaviour in the outer core region. One-electron functions \( \phi_{x,k}^{\text{corr}}(r) \), being some linear combinations of virtual orbitals, correlate to occupied orbitals \( \phi_{x}^{\text{occ}} \) (where \( x = c, v \) stands for the outer core and valence orbital indices) and are usually localized in the same space region as \( \phi_{x}^{\text{occ}} \). Therefore, the original “direct” Coulomb two-electron integrals describing the outercore-valence correlation of \( \phi_{x}^{\text{occ}} \) and \( \phi_{v}^{\text{occ}} \) can be satisfactorily reproduced by those with the pseudoorbitals, despite their localization in different space regions.
However, a two-electron integral describing the “exchange” part of the outercore-valence correlation,

\[ \int \frac{d\vec{r}' c_{\vec{r},k}^\dagger (\vec{r}') \phi_{\vec{r},c}^{\text{occ}} (\vec{r})}{|\vec{r}' - \vec{r}|}, \]

(8)
cannot be well reproduced because the valence pseudoorbitals are smoothed in the outer core region where the outer core pseudoorbitals are localized (for more theoretical details, see Ref. 4).

To overcome this disadvantage, one should use RECP’s with at least 20 electrons, e.g., 20e-GRECP\textsuperscript{27,28}. In Ref. 27, for the case of the 20e-GRECP it was also shown that the 5s, 5p pseudospinors could be frozen while still providing significantly higher accuracy than 12e-RECP’s because the valence and virtual ns and np \( (n = 6, 7, \ldots) \) pseudoorbitals in the former case already have the proper nodal structure in the outer core region.

The freezing technique discussed above can be efficiently applied to those outer core shells for which the spin-orbit interaction is clearly more important than the correlation and relaxation effects. If the latter effects are neglected entirely or taken into account within “correlated” GRECP versions, the corresponding outer core pseudoorbitals can be frozen and the spin-orbit basis sets can be successfully used for other explicitly treated shells. This is true for the \( 5p_{1/2,3/2} \) subshells in Hg, contrary to the case of the \( 5d_{3/2,5/2} \) subshells. Freezing the outer core pseudoorbitals allows one to optimize an atomic basis set only for the orbitals which are varied or explicitly correlated in subsequent calculations, thus avoiding the basis set optimization for the frozen states and reducing the number of the calculated and stored two-electron integrals. Otherwise, if the \( 5p \) shell should be correlated explicitly, a spinor basis set can be more appropriate than the spin-orbit one in a molecular calculation.

As to the Pb atom, the use of nodeless pseudospinors for valence \( 6s, 6p, \ldots \) shells leads to large (G)RECP errors but “freezing” 5s, 5p, 5d pseudospinors within 22-electron GRECP again gives 4-electron GRECP but with much smaller matching radii, therefore, its errors practically coincide with the errors of the “frozen core” approximation already.

### III. SCHEME OF “CORRELATED” GRECP GENERATION.

The GRECP method was chosen to take into account the core correlations because it allows one to reproduce very accurately electronic structure in the valence region whereas the errors of the radially-local approximation of the RECP operator (or of the RECP’s generated for only nodeless pseudospinors)\textsuperscript{4} as well as the errors of other approximations made in calculations can be more significant than the contributions from the core correlations (e.g., see Tables VI and X of Ref. 34). To take account of the latter effects, we have chosen the Fock-space relativistic coupled cluster method with one- and two-body cluster amplitudes (FS RCC-SD)\textsuperscript{37} because it has essential advantages in accounting for correlations with the core electrons whereas accurate treatment of correlations between valence electrons is not so important for the CGRECP generation stage. This method is size-consistent that is, in particular, significant for the compounds of heavy elements. The FS RCC computational scheme, in which the part of correlations from lower sectors is “frozen” in the higher Fock space sectors, is especially suitable for incorporating the most important correlations of them into CGRECP. Neglecting the higher order cluster amplitudes seems us reasonable because the core correlations give relatively small corrections to the properties determined mainly by the valence electrons. This approximation can be compared to that made in the scheme of constructing conventional GRECP’s on the base of the Dirac-Fock(-Breit) calculations despite these GRECP’s are suggested to be used in accurate correlation calculations, see Ref. 4 for theoretical details. At last, the atomic RCC-SD code\textsuperscript{37} is very efficient because it fully exploits the spherical symmetry of atoms.

The main steps of the current scheme of generation of the CGRECP’s are as follows:

1. For a considered atom, a set of occupied spinors is derived from an all-electron DF calculation for some closed shell state which is energetically close to the states of primary interest in calculations with the constructed CGRECP. The unoccupied spinors are obtained with the help of some procedure for a basis set generation (e.g., described in Refs. 11,24). Other basis set generation procedures could be also applied at this step because very large basis sets can be used in atomic calculations unlike the following molecular (G)RECP calculations. The Fock matrix and two-electron integrals are calculated in this basis set with all-electron Dirac-Coulomb or Dirac-Coulomb-Breit Hamiltonians.

2. Two equivalent FS RCC-SD calculations are carried out with the same spaces of active spinors\textsuperscript{38} and schemes of calculation. In the present work, the closed shell ground states of the Hg\textsuperscript{2+} and Pb\textsuperscript{2+} ions served as references and the Fock-space schemes were

\[ \text{Hg}^{3+} \leftrightarrow \text{Hg}^{2+} \rightarrow \text{Hg}^{+}, \quad \text{Pb}^{3+} \leftrightarrow \text{Pb}^{2+} \rightarrow \text{Pb}^{+}, \]

(9)
with electrons added in the 6s1/2, 6p1/2, 6p3/2, 6d5/2, 6d3/2, 5f7/2, 5f5/2, 5g7/2, 5g9/2 and 6p1/2, 6p3/2 active spinors of 
Hg and Pb, respectively, and removed from the 5d3/2, 5d5/2 Hg and 6s1/2 Pb spinors. Only valence electrons are 
correlated in calculation $\mathcal{V}$, whereas both the valence and core electrons are correlated in calculation $\mathcal{A}$. The active 
space should contain the spinors, for which the CGRECP components will be then constructed at step (5). The 
6d, 5f, 5g CGRECP components for Pb were constructed employing the conventional GRECP generation scheme 
with the 6s and innermore shells “frozen” after step (5). It was checked on example of Hg that this simplification 
of the generation procedure leads to negligible changes in the results of the CGRECP calculations. As a result 
of the FS RCC-SD calculations, a set of the one-body ($t^n_v$) and two-body ($t^{ab}_ij$) cluster amplitudes and ionization 
potentials ($e_m$) or electron affinities ($e_v$) is obtained. The $m$ and $v$ indices run over the active spinors occupied and 
unoccupied in the starting closed shell state, correspondingly. The $i,j$ indices in the cluster amplitudes run over the 
spinors occupied in the above closed shell state and can, additionally, include the $v$ indices. The $a,b$ indices in 
the cluster amplitudes run over the spinors unoccupied in the above closed shell state and can, additionally, include 
the $m$ indices. If the correlations of the electron in state $i$ are not considered (e.g., in calculation $\mathcal{V}$), we put the 
corresponding $t^n_v$, $t^{ab}_ij$ and cluster amplitudes to zero.

3. Differences $\Delta t_i^n = t_i^n[A] - t_i^n[\mathcal{V}]$, $\Delta t^{ab}_ij = t^{ab}_ij[A] - t^{ab}_ij[\mathcal{V}]$, $\Delta e_m = e_m[A] - e_m[\mathcal{V}]$ and $\Delta e_v = e_v[A] - e_v[\mathcal{V}]$ are calculated. 
If the absolute values of the $\Delta t_i^n$, $\Delta e_m$ and $\Delta e_v$ differences are less than some threshold ($10^{-6}$ in the present work), 
we go to step (5). If they are not, we go to step (4). In the present generation scheme, the $\Delta t^{ab}_ij$ differences are 
neglected. However, they could be later compensated with the help of the two-electron term-splitting correction for 
higher accuracy.

4. We use $\Delta t_i^n$ to rotate the spinors ($\phi$) in the basis set

$$\phi_i = \phi_i^{\text{prev}} + \sum_a \Delta t_i^a \phi_a^{\text{prev}} \quad \text{for} \quad i \notin \{v\} \quad \text{and} \quad a \notin \{m\},$$

$$\phi_v = \phi_v^{\text{prev}} + \sum_a \Delta t_v^a \phi_a^{\text{prev}}, \quad \phi_m = \phi_m^{\text{prev}} - \sum_i \Delta t_i^m \phi_i^{\text{prev}},$$

where $\phi^{\text{prev}}$ is the spinors obtained at the previous iteration. The derived spinors are then orthonormalized by the 
Schmidt procedure. The Fock matrix and two-electron integrals are calculated in the obtained basis set. We use 
$\Delta e_m$ and $\Delta e_v$ to modify the diagonal Fock matrix elements ($F_{mm}$ and $F_{vv}$) only for calculation $\mathcal{V}$

$$F_{mm}[\mathcal{V}] = F_{mm}^{\text{prev}}[\mathcal{V}] - \Delta e_m, \quad F_{vv}[\mathcal{V}] = F_{vv}^{\text{prev}}[\mathcal{V}] - \Delta e_v,$$

where $F^{\text{prev}}[\mathcal{V}]$ is the Fock matrix derived at the previous iteration. We put the nondiagonal Fock matrix elements 
for calculation $\mathcal{V}$ to zero. Then, we go to step (2).

5. The spinors and the corresponding Fock matrix elements from calculation $\mathcal{V}$ are used instead of the original spinors 
and their one-electron energies at the CGRECP generation scheme employing the procedure of the GRECP generation 
described in section IIIA

Some of the most important properties of the generation schemes of reliable RECP’s are their “basis-set-
"independence" and “correlation-method-independence". It means that extension of a one-electron basis and improving 
the level of the correlation treatment should not lead to decreasing accuracy of calculations with the used RECP. 
These properties do not always take place for the well-known RECP’s (pseudopotentials) but they are, as a rule, 
fulfilled for the shape-consistent RECP’s and GRECP’s. The case of the correlated RECP’s including CGRECP’s is, 
obviously, more critical. Nevertheless, the discussed scheme of the CGRECP generation seems us flexible enough in 
these aspects since large basis sets can be employed within the FS RCC-SD calculations of atoms (in particular, their 
quality is sufficient for the accuracy of our interest in generating the CGRECP’s for Hg and Pb, see below) whereas 
the contribution from three- and higher-body RCC amplitudes to the core correlation effects is not expected to be 

IV. ATOMIC CALCULATIONS.

Correlation structure of the Hg and Pb atoms was studied accurately in Refs. 112. It can be seen from Ref. 11 that 
at least 34 external electrons of Hg should be correlated if consistent agreement with experimental data better than 
200 cm$^{-1}$ for energies of one-electron transitions is desired for low-lying states. Such accuracy is of practical interest
in many cases (for chemistry of \(d, f\)-elements, many oxides etc.). Then, it was shown in Ref. 2 that the three-body cluster amplitudes for 12 external electrons of the mercury atom and 13 electrons of the mercury hydride molecule are required to obtain accurate results. Moreover, the polarization/relaxation of the 5\(d\) shell of Hg is rather large in chemical bonding and should be treated explicitly. We describe correlations with the “spherically symmetric” \(4f, 5s, 5p\) core shells of Hg by means of the CGRECP whereas the correlations for the 5\(d, 6s, 6p\) shells should be taken into account explicitly in the following calculations with this CGRECP. For Pb we include the correlations with the 4\(s, 4p, 4d, 4f, 5s, 5p, 5d\) shells into the CGRECP. It is in agreement with chemical intuition since Hg is a transition metal whereas the 5\(d\) shell in Pb is not so active chemically. It should be noted that the core-valence partitioning used for incorporating the correlation effects into CGRECP differs from the “innercore-outercore-valence” partitioning used in the conventional GRECP generation procedure. Therefore, those core shells which are explicitly treated with a GRECP constructed within the conventional scheme but whose correlations are taken into account at the CGRECP generation stage must be considered as “frozen” in the subsequent CGRECP calculations (see section II B and the following section for details). The states used in the FS RCC-SD calculations at step (2) of the CGRECP generation (“generator states”) are 5\(d\)\(^{3/2}\), 5\(d\)\(^{5/2}\), 6\(p\)\(^{3/2}\), 5\(d\)\(^{1}5\(d\)\(^{2}\), 5\(d\)\(^{3}6\(d\)\(^{2}\), 5\(d\)\(^{4}5\(d\)\(^{2}\), 5\(d\)\(^{5}6\(d\)\(^{2}\), 6\(s\)\(^{1/2}\), 5\(d\)\(^{3}5\(d\)\(^{2}\)\(6\)\(^{1/2}\), 5\(d\)\(^{4}5\(d\)\(^{2}\)\(6\)\(^{1/2}\), 5\(d\)\(^{5}5\(d\)\(^{2}\)\(6\)\(^{1/2}\), 5\(d\)\(^{6}5\(d\)\(^{2}\)\(6\)\(^{1/2}\), 5\(d\)\(^{7}5\(d\)\(^{2}\)\(6\)\(^{1/2}\), 5\(d\)\(^{8}5\(d\)\(^{2}\)\(6\)\(^{1/2}\), 5\(d\)\(^{9}5\(d\)\(^{2}\)\(6\)\(^{1/2}\), 5\(d\)\(^{10}5\(d\)\(^{2}\)\(6\)\(^{1/2}\), 5\(d\)\(^{11}5\(d\)\(^{2}\)\(6\)\(^{1/2}\), 5\(d\)\(^{12}5\(d\)\(^{2}\)\(6\)\(^{1/2}\) for Hg and 6\(s\)\(^{1/2}\), 6\(s\)\(^{3/2}\), 6\(s\)\(^{1/2}\)\(6\)\(^{1/2}\), 6\(s\)\(^{1/2}\)\(6\)\(^{3/2}\) for Pb. The gaussian expansions of the CGRECP’s generated following the above discussed scheme as well as of the earlier GRECP versions for Hg and Pb can be found on our website [http://www.qchem.mpipi.sb.ru/GRECPs].

To check accuracy of the generated CGRECP’s, we carried out comparative RCC and configuration interaction (CI) calculations, in which the correlations were explicitly considered only for the valence electrons. Both CGRECP and earlier GRECP versions were used in these calculations, in which the core shells were treated as frozen. We will further refer to these earlier GRECP versions with the frozen core shells as to VGRECP’s (in molecular calculations these shells are “frozen” within the VGRECP’s). Similar precision can be expected in calculations of at least vertical excitation energies for their compounds.

V. MOLECULAR CALCULATIONS.

The correlation structure for the lowest-lying states of the HgH molecule and HgH\(^+\) ion was carefully studied in Ref. 2 with the help of the RCC-SD and nonrelativistic (one-component) CC-SDT codes39,40 (the latter was used in the scalar-relativistic RCC calculations to account for three-body cluster amplitudes). A good agreement with the experimental data was attained when 19 external electrons of the HgH molecule were correlated by the RCC-SD method38 (19e-RCC-SD) with an approximate accounting for the contribution of the three-body cluster amplitudes for 13 outermost electrons and the counterpoise correction31,42 applied. The above numbers of electrons are, obviously, smaller by one for the HgH\(^+\) ion. The conventional GRECP version from Ref. 22 was used in calculations5. The aim of the calculations presented in Table III is to study how the results of the GRECP/19e-RCC-SD calculation will be reproduced in the 13e-RCC-SD calculation with the CGRECP generated for Hg in the present work. Twelve electrons are explicitly considered in calculations with both the VGRECP and CGRECP because the 5\(s, 5p\) pseudospinors of Hg are described within them by adding the Huzinaga-potential-type terms to the conventional GRECP operator (in some sense the core spinors are “frozen” with the help of the level-shift technique even when the spin-orbit basis set is employed for the valence electrons, see section II B). The same basis set as in Ref. 2 was used for the present VGRECP and CGRECP calculations. The other details of these calculations are described in Ref. 2 where they were designated as the RCC-SD-1 ones.

One can see from Table III that application of the CGRECP instead of the VGRECP in the 13e-RCC calculation allows one to improve the agreement with the GRECP/19e-RCC calculation for the vibrational frequencies up to an order of magnitude. The improvement up to two times is observed for the bond lengths (rotational constants). The errors for the dissociation energies are decreased but the errors for the transition energies are increased. However, both the errors are on the level of “chemical accuracy”. The higher-order Dunham coefficients \(w_2, x_3, \alpha_x, -Y_0\) are reproduced, as a rule, worse with the CGRECP than with the VGRECP. It should be noted that the correlations with the 4\(f\) and 5\(s\) shells of Hg were neglected in the GRECP/19e-RCC calculations. In turn, the CGRECP for Hg takes
into account these correlations. Therefore, the best suitable calculation to estimate the accuracy of the CGRECP is the 35e-RCC one. It is shown in Ref. 11, however, that the contributions from the correlations with the 4f and 5s shells mainly cancel each other.

The PbO molecule is of interest now first of all in connection with the ongoing and suggested experiments on search for the electric dipole moment of the electron on the excited \( \sigma(1) \) and \( \beta(1) \) states. In particular, calculations \(^{11,12}\) of the effective electric field, \( W_d \), seen by an unpaired electron are necessary for interpretation of the experimental results. Calculation of spectroscopic properties can be useful to search for some better scheme of populating the working state. The aim of the present calculations is to check accuracy and reliability of the CGRECP version used by us on example of the ground state of PbO, for which highly accurate experimental data are available.

We carried out 10-electron spin-orbit direct CI (10e-SODCI) \(^{45,46}\) calculations of the potential curve for the ground state of the PbO molecule (see Refs. \(^{14,15}\) for the details of such calculations). The calculations were carried out for 20 internuclear distances from 2.7 a.u. to 4.6 a.u. with interval of 0.1 a.u. Molecular spectroscopic constants were calculated by the Dunham method in the Born-Oppenheimer approximation using the DUNHAM-SPECTR code.\(^{43}\) The core of Pb was simulated with the help of the VGRECP version from Refs. \(^{12} \) and with the CGRECP version generated in the present work. Four electrons are explicitly considered in calculations with both the VGRECP and CGRECP, in which the 5s, 5p, 5d pseudospinors of Pb are “frozen” with the help of the level-shift technique (see section \(^{11,13}\)). No relativistic effects were accounted for oxygen and, besides, its 1s shell was frozen in the PbO calculations. Thus, only four electrons of lead and six electrons of oxygen were explicitly correlated. The same basis set was used for the VGRECP and CGRECP calculations. We estimated that the counterpoise corrections for the \( ^3P_0 \) and \( ^3P_2 \) states of Pb and for the \( ^3P \) state of oxygen are less than 0.02 eV for all the considered internuclear distances. The calculations at higher level of accuracy were not carried out because the corresponding SODCI calculations became very consuming. Therefore, the counterpoise corrections were neglected when the spectroscopic constants were calculated. The obtained results are presented in Table IV. One can see that both results are in reasonably good agreement with the experimental data. The largest improvement (about six times) for the CGRECP with respect to VGRECP is observed for the vibrational frequencies. Similar improvement was also observed for the frequencies in HgH. The errors for the dissociation energy (approximately 2 kcal/mol for breaking the double bond) are comparable in the used basis sets, insufficient level of accounting for the correlation in the above restricted CI calculations, etc. The agreement for other spectroscopic constants with the experimental data is improved in about two times when the CGRECP is applied instead of the VGRECP. Similar result was also obtained for the bond lengths in HgH.

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TABLE I: The experimental transition energies between the low-lying states of the mercury atom and its cations are taken from Ref. 5. The absolute errors in the transition energies from 12-electron FS RCC-SD calculations with the VGRECP, CGRECP and all-electron Dirac-Coulomb (DC) Hamiltonian in the [7, 9, 6, 7, 7] correlation basis set from Ref. 2 are calculated with respect to the transition energies from 34-electron FS RCC-SD calculation with all-electron DC Hamiltonian. All values are in cm$^{-1}$.

| State (leading conf., term) | Transition energies | Absolute errors with respect to DC/34e-RCC |
|----------------------------|---------------------|------------------------------------------|
| 5d$^{10}$6s$^2$(S$^0_0$) → |                     |                                           |
| 5d$^{10}$6s$^2$6p$^1$(P$^0_0$) | 37645               | -263                                      |
| 5d$^{10}$6s$^2$6p$^1$(P$^1_1$) | 39412               | -326                                      |
| 5d$^{10}$6s$^2$6p$^1$(P$^2_1$) | 44043               | -534                                      |
| 5d$^{10}$6s$^2$6p$^1$(P$^3_1$) | 54069               | -650                                      |
| 5d$^{10}$6s$^2$(2S$^1_1$/2)   | 84184               | -665                                      |
| 5d$^{10}$6s$^2$(2P$^1_1$)      | 51485               | -510                                      |
| 5d$^{10}$6p$^3$(2P$^3_3$)      | 60608               | -793                                      |
| 5d$^{10}$6p$^3$(S$^0_0$)       | 151280              | -1087                                     |

$^a$This number is smaller by one or two for Hg$^+$ or Hg$^{2+}$ ions, respectively.

TABLE II: The experimental transition energies between low-lying electronic states of the lead atom are taken from Ref. 50. The absolute errors of all-electron Dirac-Coulomb (DC), VGRECP and CGRECP calculations with the help of the RCC and CI methods for 4 and 36 explicitly correlated electrons in the [7, 6, 6, 4, 4]/[3, 5, 3, 2] basis set from Ref. 2 are calculated with respect to the experimental data. All values are in cm$^{-1}$.

| State (leading conf., term) | Absolute errors with respect to the experimental data |
|----------------------------|---------------------------------|
| 6s$^2$6p$^2$6p$^1$)(P$^0_0$) |                     |
| 6s$^2$6p$^2$6p$^1$6p$^1$)(P$^1_1$) | 7819               | -807                                      |
| 6s$^2$6p$^2$6p$^1$6p$^1$)(P$^2_1$) | 10650              | -752                                      |
| 6s$^2$6p$^2$6p$^1$6p$^1$)(D$^2_2$) | 21457              | -1707                                     |
| 6s$^2$6p$^2$6p$^1$6p$^1$)(S$^0_0$) | 29466              | -1553                                     |

$^b$36 electron FS RCC-SD calculation with valence CI Correction (VCIC$^b$) as the difference in the total energies from 4e-CI and 4e-FS RCC-SD calculations accounting approximately for the three- and four-body cluster amplitudes for four valence electrons.

TABLE III: Spectroscopic constants of the lowest-lying states of the HgH molecule and HgH$^+$ ion from 13 and 19 electron$^a$ RCCSD calculations with the GRECP, VGRECP and CGRECP in the H (8, 4, 3)/[4, 2, 1] and Hg (14, 12, 9, 3, 2)/[7, 7, 4, 2, 1] basis set from Ref. 2. All the results are corrected by counterpoise corrections calculated for the Hg 6s$^2$ state. $R_e$ is in Å, $D_e$ in eV, $Y_{02}$ in 10$^{-6}$ cm$^{-1}$, other values in cm$^{-1}$.

| HgH (σ$^2$g$^2$) 2Σ$^+_1/2$ | R$_e$, w$_e$, D$_e$, B$_e$, w$_{x_e}$, α$_{x_e}$, $Y_{02}$ |
|----------------------------|-----------------------------------------------------|
| VGRECP/13e-RCC             | 1.799 1575 0.35 5.76 56 0.262 312                   |
| CGRECP/13e-RCC             | 1.705 1595 0.34 5.78 59 0.265 308                   |
| HgH$^+$ (σ$^2$g$^2$) 2Σ$^+_1/2$ | R$_e$, w$_e$, D$_e$, B$_e$, w$_{x_e}$, α$_{x_e}$, $Y_{02}$ |
| VGRECP/12e-RCC             | 1.596 2037 2.67 6.60 39 0.200 279                   |
| CGRECP/12e-RCC             | 1.593 2070 2.73 6.63 40 0.200 273                   |
| HgH$^+$ (σ$^2$g$^2$) 2Π$^1/2$ | R$_e$, w$_e$, T$_e$, B$_e$, w$_{x_e}$, α$_{x_e}$, $Y_{02}$ |
| VGRECP/13e-RCC             | 1.586 2067 24157 6.68 39 0.203 281                  |
| CGRECP/13e-RCC             | 1.583 2104 24324 6.71 41 0.203 274                  |

$^a$These numbers are smaller by one for the HgH$^+$ ion.
TABLE IV: Spectroscopic constants for the ground state of the PbO molecule from 10-electron SODCI calculations with the VGRECP and CGRECP in the Pb (22, 18, 12, 6, 5)/[5, 6, 4, 3, 1] and O (14, 9, 4, 3, 2)/[6, 5, 4, 3, 2] basis set. $R_e$ is in Å, $D_e$ in eV, $\alpha_e$ in $10^{-3}$ cm$^{-1}$, $Y_{02}$ in $10^{-6}$ cm$^{-1}$, other values in cm$^{-1}$.

|          | $R_e$ | $w_e$ | $D_e$ | $B_e$ | $w_e x_e$ | $\alpha_e$ | $-Y_{02}$ |
|----------|-------|-------|-------|-------|-----------|------------|-----------|
| VGRECP/10e-SODCI | 1.943 | 715   | 3.79  | 0.301 | 3.27      | 1.73       | 0.213     |
| CGRECP/10e-SODCI | 1.933 | 720   | 3.77  | 0.304 | 3.42      | 1.84       | 0.216     |
| Experiment$^a$  | 1.922 | 721   | 3.87  | 0.307 | 3.54      | 1.91 (0.223)$^a$ |

$^a$Cited in Ref. 51 as uncertain.