Comments on “Effective Core Potentials” [ M. Dolg, Modern Methods and Algorithms of Quantum Chemistry (Ed. by J.Grotendorst, John von Neumann Institute for Computing, Jülich, NIC Series, Vol.1, ISBN 3-00-005618-1, pp.479-508, 2000) ].

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(March 31, 2022)

Abstract

The recent paper of M. Dolg is discussed and his critical remarks with respect to the Generalized Relativistic Effective Core Potential (GRECP) method are shown to be incorrect. Some main features of GRECP are discussed as compared with the “energy-consistent/adjusted” pseudopotential and with the conventional shape-consistent RECP.

I. INTRODUCTION

The discussed paper of M. Dolg deals with the relativistic effective core potential (RECP) methods including the model potential and pseudopotential (PP) techniques. The shape-consistent RECP method as a PP version is compared with the “energy-adjusted” PP (EAPP) and the “energy-consistent” PP (ECPP) developed by Stuttgart’s group (e.g., see [1,2] and references in the discussed paper by M. Dolg). In their semiempirical version, EAPP, partial potentials are fitted to reproduce the experimental atomic spectrum. In the ab initio approximation, ECPP (earlier also called energy-adjusted PP), “valence energies” (i.e. sums of ionization potentials and excitation energies) for a group of low-lying states are fitted to the corresponding energies of the same states in all-electron approximations like Hartree-Fock, Wood-Boring or Dirac-Fock in a least-squares sense with the help of the ECPP parameters. It means that only some special combinations of the matrix elements of a (non-,quasi-)relativistic Hamiltonian are fitted by the ECPP and EAPP Hamiltonians with the help of the one-electron radially local PP operator. When considering below both ECPP and EAPP versions we will write ECAPPs or Stuttgart PPs.

The radially local operator is also used in the shape-consistent RECPs and some new non-local RECP terms are added in our Generalized RECP (GRECP) version [3-16], which we consider as a development of the shape-consistent RECP method. The underlying idea traced in our papers concerning the GRECP approximation is in simulating the one- and two-electron parts of an original Dirac-Coulomb (in prospect, Dirac-Coulomb-Breit) Hamiltonian with the accuracy which is needed and sufficient for calculation of physical and chemical properties (and processes) in heavy-atom molecules with a given accuracy. A paramount
requirement is that such a simulation should provide maximum possible savings for consequent molecular calculations with GRECPs.

As is confirmed in all our test calculations and not only in our theoretical analysis, the GRECP Hamiltonian in the form used in papers by Mosyagin et al. (1997) and (2000) (which are criticized by M. Dolg) more accurately reproduces the Dirac-Coulomb Hamiltonian in the valence (V) region as compared with other tested RECP and Stuttgart PP versions employing the radially local operator. Phrase “in the valence region” means that the occupation numbers of the outer core (OC) shells, \( n^{\text{occ}}_{\text{OC}} \), are not considerably changed in studied states as compared with the OC occupation numbers of the configurations used in the GRECP generation (i.e. \( \Delta n^{\text{occ}}_{\text{OC}}<1 \)). Thus, only relaxation and dynamic correlation effects are suggested to take place in the OC shells.

We have emphasized this property of the GRECP Hamiltonian already in the introduction of paper [7]. It is noted in the abstract of our theoretical paper (1997,1999) [10] where a very detailed analysis of features of the shape-consistent RECP method including the GRECP approximation is given. We consider the GRECP version for Hg used in [7,11] as reliable for atomic and molecular calculations of the states in which the OC shells of Hg are completely occupied in the leading configurations if accuracy of a few hundreds wave numbers for transition, dissociation etc. energies is required. In papers [5,10], some other improvements of the RECP method are suggested in order to provide minimal computational efforts in accurate RECP calculation of wide range of excitations and properties in systems containing arbitrary heavy atoms including transition metals, lanthanides and actinides. We, obviously, will not repeat here the theoretical analysis of the shape-consistent RECP method and will give only some necessary details which have direct attitude to the criticized points.

The goal of this paper is mainly to compare features of the GRECP and other RECP versions including Stuttgart PPs rather than to reply on Dolg’s claims. These comments can be also useful for reading them before paper [10].

II. GENERAL COMPARISON OF DIFFERENT RECP VERSIONS

The discussed GRECP version is assumed to be efficiently used when excitations and chemical bonding take place in the V region whereas only dynamic correlation and relaxation (polarization) are considered in the OC region. Therefore, interactions between/with valence and outer core electrons are simulated on the basis of the following principles:

First, for selected subspaces of the OC and V shells, the matching radii \( R_c \) for the regions of the spinor’s smoothing are chosen to be as small as possible in order to reduce the errors of reproducing the original two-electron integrals (in further reducing the matching radii, partial potentials become too singular to be approximated by gaussians and used in RECP calculations, for details see [10]). When using the GRECP operator in calculations of the same states as with the Dirac-Coulomb Hamiltonian, the OC, V and virtual pseudospinors coincide with the large components of the original Dirac spinors after the matching radii with significantly higher accuracy than in the cases of using the conventional RECP operator [2,11]. In a result (it is very important), the radius of the “unphysical” GRECP terms (the partial potentials \( U_{nij}(r) \) contain the contribution from the Coulomb and exchange interac-
tion with the IC electrons, the contribution from relativistic effects, and the contribution from smoothing the original spinors) only slightly larger than the outermost matching radius \( R_{c}^{\text{max}} \) for pseudospinors. This is direct consequence of generating different partial potentials, \( V_{nlj}(r) \), for the corresponding OC and V (and virtual) pseudospinors with the same \((lj)\). It is shown in [16] that difference between the OC and V potentials with the same \((lj)\) can not be eliminated with the help of any special kind of smoothing the corresponding OC and V spinors without substantial decrease in accuracy for transition energies, up to an order of magnitude. Thus, when reducing the matching radii, which are usually close to each other, we reduce the radius of unphysical terms in the corresponding atomic effective Hamiltonian. The independent smoothing the OC and V (and, in principle, some virtual) spinors with polinomials give us sufficient flexibility to generate smooth enough OC and V pseudospinors as well as their partial potentials.

The GRECP is a “matching radii-specified” (or “space-driven”) method of approximation (see [10]) contrary to the energy-adjusted/consistent PPs which are “selected valence energy-based” (or “energy-driven”). The “space-driven” RECPs are substantially better justified from the theoretical point of view [11] and, in general, they more properly reflect the relaxation/polarization properties of the inner core region in a heavy element.

Second, the non-local terms with projectors on the outer core pseudospinors in the GRECP operator give us an important possibility to reproduce the original OC and V orbital energies and the (most important) nondiagonal Lagrange multipliers [14], which together with the Hartree-Fock (Coulomb and exchange) electronic terms derived on pseudospinor densities constitute the one-electron part of the effective (model) Hamiltonian. Therefore, the one-electron part of the Hamiltonian in the V region can be reproduced very accurately (see section “Theory” in [14] for more details). The orbital energies are used in denominators of the Möller-Plessett perturbation theory (PT) accounting for correlation etc. Otherwise, some other combinations of matrix elements of an original Hamiltonian can be reproduced in the model one instead of the orbital energies and nondiagonal Lagrange multipliers. (In particular, those one-electron energies can be exactly simulated which are more appropriate, e.g., for the Epstein-Nesbet PT. However, the partial potentials have additional “tails” in such cases because of the use the inverted Hartree-Fock equations for their generation and the radius of the unphysical (G)RECP terms is thus enlarged. One should remember that the tail behaviour of orbitals is determined by their orbital energies. The distinction in using differently determined one-electron energies is not very essential if the corresponding original Coulomb and exchange two-electron integrals are accurately reproduced by those with pseudospinors as is for small matching radii [10].)

We are “fitting” the Hamiltonian matrix elements in the valence region first of all and not some their combinations of a special kind likewise the valence energies. It is sufficient to use a very small number of DF configurations for the GRECP generation, with the basic requirements: \(a)\) they should have the same configurational structure in the core region as the states of the “atom in a molecule” studied in the GRECP calculations; \(b)\) they should contain all the spinors required for the generation of the corresponding partial potentials.

Obviously, it is possible to fit transition or valence energies for a group of states with the help of the energy-consistent/adjusted PPs having appropriate number of fitting parameters. Certainly, it is not equivalent to the simulation of all the important Hamiltonian matrix elements on a needed level of accuracy in order to describe a possible variety of perturbations.
in the valence region of a considered element with a given accuracy. All the one- and two-electron matrix elements of the original valence Hamiltonian should be appropriately reproduced for the element to be used for accurate calculations of a wide range of applications including excitations and chemical bonding with arbitrary atoms and geometries. Besides, fitting the valence energies prior to the orbital energies, give no any advantages, in particular, in reproducing the variety of physical and chemical properties which cannot be calculated from potential curves or surfaces. The “steady” simulation of the valence Hamiltonian can be done on the basis of the “space-driven” shape-consistent RECP generation scheme.

The conventional RECP operator with the shape-consistent spinor smoothing suggested by K.Pitzer’s group (1979,1977) gives no flexibility in fitting shapes and orbital energies simultaneously for the OC and V spinors with the same \((lj)\). When the OC (pseudo)spinors are used in their RECP generation scheme for a given \((lj)\), the “effective matching radii” for other (V and virtual) pseudospinors with the same \((lj)\) are, in fact, larger than those for the OC pseudospinors. The same problem take place when the partial potentials are generated for the V (pseudo)spinors and then applied for the OC shells with the same \((lj)\). Therefore, in general (see [10] for more theoretical details), the Hamiltonian matrix elements are not so accurately reproduced as in the case of GRECPs. By other words, the radius of “unphysical” terms in a conventional RECP is substantially larger than the matching radii (contrary to the GRECP case as one can see from our papers and the foregoing text).

In turn, the ECAPP generation schemes take no care about smooth pseudoorbitals (pseudospinors) and matching radii when putting simulation of some valence energies and generation of smooth partial potentials on the first place. (A small number of gaussians in the ECAPP expansion is, in fact, equivalent to smooth partial potentials). The result is similar to that in the case of the conventional shape-consistent RECP. Additional disadvantages of ECAPPs are a poor theoretical justification and technical complexity in fitting a large number of valence energies. When taking account of correlations in ECPP calculations, the valence energies for the correlated states should be fitted as well if a high computational accuracy is required. It should be done as a pay for the absence of matching radii for the ECPP pseudospinors. Moreover, being one-electron potentials of a special (radially local) type, ECAPPs generated for a fixed number of explicitly treated electrons can not provide arbitrarily high accuracy even for reproducing the one-electron part of the valence Hamiltonian [10], not to mention the two-electron part. Besides, how many transition/valence energies between/for correlated states should be fitted for reliable reproducing a required (large) number of the two-electron integrals with some needed accuracy? Hundreds? Or maybe thousands? Can it be efficiently applied in practice? Will it provide a “proportional” (even) level of errors for the one- and two-electron integrals as is in the case of GRECPs? Should not forget that the ECAPPs employ the conventional RECP operator that is not so flexible as the GRECP one [14,16]. We can also remind here about those properties which cannot be calculated from potential curves or surfaces. Why will these properties be accurately reproduced with the help of ECAPPs?

In the optimization of the parameters of partial potentials \(V_{nlj}(r)\) one can produce compact gaussian expansions for the ECAPPs when fitting directly some selected valence ener-
gies. Is this a real advantage? The compactness in the gaussian expansions of the partial potentials does not ensure the smoothness of pseudoorbitals (pseudospinors). Moreover, the radius of unphysical terms in such a PP is inevitably larger than in the RECPs in which a large set of gaussians is employed to fit quite singular behaviour of numerical potentials \((V_{nlj}(r) - N_{\text{core}}/r)\) close to the matching points thus reducing their effective radii (see Figure 2 in [10]). It is very widely known that the effort in the calculation \((\sim N^4)\) and transformation \((\sim N^5)\) of two-electron integrals (where \(N\) is the number of basis functions) is always substantially higher than in calculation of the RECP integrals \((\sim N^2 \cdot N_{\text{RECP}}, \text{where} N_{\text{RECP}}\) is the number of terms in the used RECP expansions) for all the known RECP versions including GRECPs when appropriately large basis sets are employed for precise calculations. Again we should emphasize that in spite of the rather complicated form of the GRECP operator, the main computational effort in calculating matrix elements with GRECPs is caused by the standard radially local operator which is also the main part of the shape-consistent RECP and ECAPP operators, and not by the non-local GRECP terms. Thus, the additional efforts in calculations with GRECPs are negligible as compared with the cases of using the conventional RECPs and PPs if comparable gaussian expansions are used for the partial potentials.

Summarizing, what is the computational utility in generation of compact RECPs and PPs? Maybe much more important is that their accuracy should be in agreement with the number of explicitly treated electrons? Obviously, the smooth shapes of pseudospinors in the atomic core are more important than smooth partial potentials. The smooth pseudospinors can be accurately approximated with a relatively small number of gaussian functions. A possibility to generate the partial potentials after constructing pseudospinors (and not simultaneously) when inverting the Hartree-Fock equations following Goddard III (1968) [17] is very convenient from the computational viewpoint. Due to these features, the RECP generation scheme by K.Pitzer’s group is very effective in practice. It is always better to have a possibility to split solution of a complicated problem on a few consequent steps. That is the reason why we prefer the scheme of K.Pitzer’s group and not that proposed by Durand & Barthelat (1975) in their classical paper [18], where the idea of the shape-consistent ECP method was first suggested. The ECAPP generation scheme is in many aspects close to the ECP generation scheme by Durand & Barthelat.

Our first comparisons of RECPs in [7] were done in the one-configurational approximation because only recently we have obtained an opportunity of employing very efficient atomic Relativistic Coupled Cluster (RCC) [28] code for reliable correlation structure calculations with both Dirac-Coulomb and (G)RECP Hamiltonians [11]. The advantage of the former comparison is in the use of the finite-difference method (i.e. spinors (orbitals) are varied in the numerical form) and therefore, the DF (HF) calculations are independent of the finite basis sets errors. In the latter case, one has a possibility to use very large basis sets thus minimizing dependence of the final results on a special choice of a basis set. Besides, there are almost no subjective dependences in RCC calculations from a special selection of configurations (reference spaces, truncation thresholds, etc.) that is very important for correct comparison of different effective Hamiltonians with original. Our statements in [7] concerning the accuracy of the GRECP Hamiltonian were done on the bases of one-configurational calculations in the \(jj\)-coupling scheme and of the theoretical analysis presented in [10]. They
are completely confirmed in first correlation calculations of Hg \[11\], Pb \[14\] and TlH \[13\]. Besides, the examined energy-adjusted PPs were found in our tests to be less accurate in general than the shape-consistent RECP versions generated by other groups.

III. REPLY ON REMARKS OF M. DOLG

Below Dolg’s remarks from the discussed paper and our answers are given. All Dolg’s quotations are taken from section 5.3 “Limitations of accuracy” in the same order as in the discussed paper unless the opposite is explicitly stated.

To minimize problems with ambiguous treatment of the quotations when extracting them from a context, the whole text of section 5.3 is presented in Appendix A.

1. See Table 1 in the Dolg’s paper.

* Our remarks:
The frozen core approximation is underlying for all the known ECP methods, both nonrelativistic and relativistic. Therefore, the accuracy of the (R)ECPs can not be considered as higher than that of the frozen core approximation unless some special corrections like the Core Polarization Potential (CPP) or our Self-Consistent (SfC) terms are used. Moreover, the smoothing of the orbitals (spinors), incorporating the relativistic effects, etc. will further increase the RECP errors. In Table I, we have compiled the errors of the new ECPP with 54 adjustable parameters from Table 1 in the Dolg’s paper together with the frozen core approximation errors calculated by us. The HFD code \[22\] is used in the corresponding Dirac-Fock all-electron and frozen core calculations with the point nuclear model for the states averaged over the nonrelativistic configurations. Obviously, having 54 adjustable parameters in the ECPP, one can use them to fit exactly 54 valence energies. However, the accuracy of the generated PP should not be estimated by the errors in reproducing the fitted energies. The valence energies which were not used in the fitting procedure or other properties must be used for the PP testing because the basic requirement of any fruitful simulation is a transferability of a model Hamiltonian to the cases which were not used when constructing this Hamiltonian. Although the number of states which is of interest for electronic structure calculations of an atom is usually not too large to allow one to fit all of them, this number is dramatically increased in the case of its chemical bounding with a multitude of other atoms.

Therefore, the accuracy of the new ECPPs can not be derived from Tables 1 and 2 in the Dolg’s paper and additional independent testing is necessary. Unfortunately, we can not do this because we do not have the parameters of his new ECPPs (see \[23\]).

2. Dolg:
Tables 1 and 2 demonstrate that for very special cases like Hg, with a closed $5d^{10}$-shell in all electronic states considered, a small-core energy-consistent pseudopotential using a semilocal ansatz reaches an accuracy of 10 cm$^{-1}$, which is well below the effects of the nuclear model, the Breit interaction or higher-order quantum electrodynamical
contributions. We also note that differences between results obtained with a frequency-dependent Breit term and the corresponding low-frequency limit amount to up to 10 cm$^{-1}$. Moreover, the quantum electrodynamic corrections listed in tables 1 and 2 might change by up to 20 cm$^{-1}$ when more recent methods of their estimation are applied [24,25].

* Answer:

The first part of the quotation is commented in the previous item and in Section I. Some special remarks can be made with respect to the Breit effect. The replacement of the two-electron Coulomb-Breit interaction by the two-electron Coulomb interaction ($1/r_{12}$) plus one-electron PP operator in the PP Hamiltonian is not justified by M. Dolg. The contribution from the (frequency-dependent) Breit interaction was evaluated in the first-order perturbation theory (PT1). However, the Breit interaction is very strong close to a heavy nucleus. Therefore, the wave function in its neighborhood is seriously perturbed by the Breit interaction and the higher PT orders by correlation should be considered (to describe the core relaxation) for appropriate accounting for the Breit correction [26]. In particular, the random phase approximation can be used keeping only the first-order perturbation on the Breit interaction, in which it is correct when accounting for the quantum electrodynamic (QED) effects. As is shown in [24,27], the core relaxation can reduce the final Breit correction by an order of magnitude. Did Prof. Dolg perform similar analysis when generating the ECPPs for Hg? After that, what is the need to take account of the QED effects in the framework of the ECPP when they give an order of magnitude smaller contribution than the ECPP errors arising from the radially local form of the ECPP operator? What is the profit (advantage) in such an accounting for the Breit and QED effects?

Those “improvements” are done by Prof. Dolg in the ECAPP method which can be done easily and not those which should be done first of all. When developing the GRECP method, we are eliminating at first its largest errors, then errors of the next level of magnitude and so on, step-by-step. The theoretical analysis of the GRECP errors is always done, thus justifying the approximations made by us.

At last, it would be excellent to perform molecular calculations on a level of accuracy of 100 cm$^{-1}$ for transition, dissociation, etc. energies systematically but the modern correlation methods, codes and computers do not allow one to do this because of the high computational cost. Our goal on the nearest future is to generate the GRECPs with inherent errors close to (or below than) 100 cm$^{-1}$ for the valence energies when treating minimal number of electrons explicitly. In molecular GRECP calculations, it allows one to attain accuracy within a few hundred wave numbers for the energies of interest reliably and with minimal efforts.

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1 Papers within the quotations are cited according the list of references in the present comments and the numbers of tables are original.
3. Dolg:

“Therefore, it is important to state exactly which relativistic all-electron model the effective core potential simulates and, when comparing effective core potentials of different origins, to separate differences in the underlying all-electron approach from errors in the potential itself, e.g., due to the size of the core, the method of adjustment or the form of the valence model Hamiltonian.”

* Answer:

It is true. As one can see from our papers, we are carefully analyzing the sources of errors in our GRECP versions. We “state exactly which relativistic all-electron model the effective core potential simulates”, etc. Moreover, we consider as our duty to present all the necessary details concerning all the GRECPs which were used in our papers. Being requested, the GRECP parameters can be received, in particular, by email.

However, it is not in our responsibility “to separate differences in the underlying all-electron approach from errors in the potential itself” for PPs and RECPs generated by other groups. How can we separate errors of the Wood-Boring approximation from the ECAPP fitting errors without knowledge of all the details of fitting, without having the required codes, and without doing some test calculations with these codes? Besides, why must we do this? The responsibility for such an analysis is on those who have generated these PPs and RECPs.

We have written in [11]:

“...”

Weis and we have written in [11]: “It should be noted that the energy-adjusted pseudopotential (PP) tested in the present paper was generated by Häussermann et al. [2] using the results of the quasirelativistic Wood-Boring [29] SCF all-electron calculations as the reference data for fitting the spin-orbit averaged PP parameters. A new 20e-PP for Hg was generated recently by fitting to the Dirac-Fock-Breit reference data [30], but we do not have the parameters of this PP.

The energies of transitions between the $6s^2$ and $6s^16p^1(3P, 3P_1, 3P_2)$ states in the 20e-PP/MRCI calculations employing the CIPSO method [31] are within 100 cm$^{-1}$ of experiment (see Table 6 in [4] or Table 2 in the present paper). However, the energy-adjusted PP does not account for the contributions from correlations with the $4f$ shell, and the basis set used does not contain $h$-type functions. One can see from Tables 1 and 2 that the contributions of the two effects to these transition energies are up to 284 cm$^{-1}$ and 247 cm$^{-1}$, respectively. The good 20e-PP/MRCI/CIPSO results are probably due to fortuitous cancellation of several contributions: the inherent PP errors (e.g., the $6s^16p^1(3P_0, 3P_1, 3P_2)$ splitting is overestimated by 1014 cm$^{-1}$ because of the features of the spin-orbit simulation within the LS-based version of the energy-adjusted scheme, see Table 4 in paper [7]), the neglect of correlations with the $4f$ shell, the basis set incompleteness, etc. A similar situation holds for

See Ref. [23] for more details.
transitions between the $6s^1$ and $6p^1(2P_{1/2},2P_{3/2})$ states of Hg$^+$, but errors of the 20e-PP/MRCI/CIPSO calculations relative to experimental data reach a level of 1000 cm$^{-1}$ in this case.”

Is it not correct? Similar analysis can be found in our previous paper [7] criticized by M. Dolg. M. Dolg many times claimed that our test results with their 20e-PP in [2] are wrong. Where can we find his publication with the confirmation of these claims? However, let us get back to the paper of M. Dolg. Why is the information about the states used in the valence energy fitting in the ECPP generation not even presented there? Where are the ECPP parameters? As is mentioned above, we have no a possibility to check the real quality of these new ECPPs (see [23]).

4. Dolg:
“In this context we want to point out that the seemingly large errors for energy-adjusted pseudopotentials reported by Mosyagin et al. [7,11] are mainly due to the invalid comparison of Wood-Boring-energy-adjusted and Dirac-Fock-orbital-adjusted pseudopotentials to all-electron Dirac-Fock data, i.e., differences in the all-electron model are considered to be pseudopotential errors.”

* Answer:
Although “the correct relativistic all-electron Hamiltonian for a many-electron system is not known”, the Dirac-Coulomb Hamiltonian is preferred over the Wood-Boring one. Moreover, for an “RECP user” the level of the PP errors with respect to the most accurate relativistic Hamiltonian (among the known ones) is much more meaningful than the question whether the PP errors are due to the unsatisfactorily fitting procedure of the ECAPPs (the small number of parameters, incompleteness of the PP operator, etc.) or due to the poor all-electron reference data used for this fitting. Therefore, the comparison of the all-electron Dirac-Coulomb data with the Wood-Boring-fitted PP results is correct in papers [7,11], whereas the manner of comparison of the all-electron Wood-Boring data with the Dirac-Fock-based GRECP results in Table XVII from [7] by M. Dolg is not valid. The (G)RECP and PP results are given in [7] only in order to show “the range of the dispersion of the data”. Besides the absence of equivalence in the used basis sets, the Wood-Boring approximation is an additional source for the distinctions between the all-electron and GRECP molecular data in this table (see also the last item in this section for more details). The question is also arise how M. Dolg and co-authours can attain an “excellent agreement” (see abstract of [2]) with the experimental data in their previous papers with the help of the Wood-Boring fitted PPs.

5. Dolg:
“It is also obvious from the compiled data that the accuracy of the valence model Hamiltonian is also a question of the number of adjustable parameters.”

* Answer:
We are very satisfied that Prof. Dolg at last have recognized the fact of importance of the number of the adjustable parameters because probably all the ECAPPs generated
before had small number of the parameters. The problem is only that the ECAPP is a one-electron operator and the original Hamiltonian contains the two-electron interactions as well. How is Prof. Dolg planning to reproduce the two-electron part when fitting the ECAPP parameters?

6. Dolg:

“Claims that such very high accuracy as demonstrated here can only be achieved by adding nonlocal terms for outer core orbitals to the usual semilocal terms [7,11] appear to be invalid, at least for energy-consistent pseudopotentials.”

* Answer:

We have revised again our papers but could not find the text which could be interpreted by such a manner as it is done in the Dolg’s paper. Can Prof. Dolg show the places in our papers where we have written so? The most debatable phrase from our papers which can be associated with the above Dolg’s quotation is “…The larger errors for RECPs [21,2] are mainly due to the neglect of the difference between the outer core and valence potentials in these RECP versions (see [10,6] for details).” We have written it on p. 674 of our joint paper [11] with the Tel Aviv group but this phrase is in the responsibility of the authors of the present comments. However, “larger errors” means here “larger level of errors” (it is clear from the context below this phrase where we clarify the origin of the errors for our particular calculations and for the used 20e-PP for Hg). Nevertheless, we are ready to recognize that in the case of the 20e-PP for Hg [2] the main contribution to the errors in the transition energies compiled in Table 3 of [11] is due to a bad quality of the used fitting principles and/or incompetent their application in [2] rather than due to the neglect of the difference between the outer core and valence potentials in this PP, if such a reformulation is more acceptable for authors of [2].

Obviously, some errors in transition energies can be smaller for an ECAPP, especially, if these energies are fitted when generating the ECAPP. We have pointed out earlier, that the ECAPPs should be checked for those transitions or properties, which were not fitted during the ECAPP generation. Test calculations should be performed with different numbers of correlated electrons and with a good quality of accounting for correlation. A “minimal completeness” of the basis sets is also required.

As to the importance of the nonlocal terms and to the phrase “This error could be reduced further upon using a smaller core, but the efficiency of the approach would be sacrificed.” written by Prof. Dolg a few lines above, we should remind the following. Already in paper [4] we have emphasized that when freezing the OC pseudospinors, the corresponding nonlocal GRECP projectors are not involved in calculations. However, the accuracy can be very high if partial potentials are generated for nodal V pseudospinors and not for OC ones thus taking into account the difference between the V and OC potentials contrary to the standard RECP case. Therefore we considered this frozen core scheme as a special GRECP version. We have pointed out later (e.g., see [10]) about similar alternatives with respect to other our additions (“self-consistent” and “spin-orbit” terms) to the conventional radially local operator. Obviously, the same (freezing) procedure can be applied when more core shells are included into the
space of explicitly treated electrons. Freezing then the innermost shells of them, one again can remove the nonlocal GRECP terms because the differences between the partial potentials for the innermost nodeless pseudospinors and the next pseudospinors with the same \((l_j)\) (but having one node) are the most essential to be taken into account. However these cases are not computationally interesting because such RECP are of interest for the modern correlation structure calculations which can provide a required accuracy when treating as small number of electrons explicitly as possible. The latter is our main purpose. That is why we prefer to change the functional form of the RECP operator, to insert core correlations to GRECPs etc. The only problem is to do this properly, by a “theoretically-consistent” way, involving appropriate functional forms. And this should be done when solving step-by-step the most actual problems, i.e. eliminating first the sources of the largest errors with minimal complication in the resulting RECP calculations. Accounting for the (high PT order) QED and other effects within an RECP is meaningless if they have smaller order of magnitude than inherent errors of the RECP under consideration.

7. Dolg:

"Moreover, additional nonlocal terms obviously do not improve the performance for atomic states with a 5d⁹ occupation"

* Answer:

It is not true. M. Dolg did not present any his results of calculations with GRECPs or any theoretical analysis. As we know from our correspondence with him, similar work have not been performed by him at all. Therefore, his conclusions are made only on the basis of our results given in [7]. However, our results and conclusions in [7] are opposite. In this connection, the adverb “obviously” is very funny.

8. Dolg:

"or in molecular calculations (cf., e.g., tables III and XVII in Mosyagin et al. [7]).”

* Answer:

Concerning the molecular GRECP calculations, the first GRECP/MRD-CI results for spectroscopic constants in TiH [13] again lead to opposite conclusions. Some other GRECP/MRD-CI and GRECP/RCC-SD calculations on HgH, TiH and PbH are in progress now. As to the spin-orbit-averaged (G)RECP/SCF and PP/SCF results on HgH presented in table XVII of [7], we are forced to repeat that our HgH calculations were performed there in order to study “the range of dispersion of the data” because for the one-electron RECP and GRECP operators it “is important information to estimate the accuracy of the RECP approximation both for one-configurational and for highly correlated calculations of HgH and HgH⁺ molecules” (see p. 1121 in [4]). The above mentioned Dolg’s excerption is certainly the top analytical result in the commented paper dealing with the pseudopotentials. Following its logic pattern, we can call this by a pseudoresult (and moreover, the results obtained with effective potentials can be analogously called by effective results for “sake of brevity”).

In fact, almost all that we have written in these comments was written in our papers earlier and we only have concentrated here on some underlying principles of our approach
as compared to other RECP methods. We regret that our papers have occurred to be so difficult for reading that Prof. Dolg could not clarify the principles and features of the GRECP method.

We should add that some more remarks could be given concerning the application by Stuttgart group of the core polarization potential together with ECAPPs, their “idea to fit exclusively to quantum mechanical observables like total valence energies” (see the discussed paper), the features of the ECAPP operator, actions to avoid admixture of the inner core states which are occupied by the electrons eliminated from calculations etc. Are the valence energies obtained from the Dirac-Fock-Breit equations observable? Without a good theoretical justification of the transferability and proper application of these very progressive ideas to other problems, the result can be unsatisfactory. This we have seen on example of application of the Wood-Boring approximation to the ECAPP generation. Moreover, when developing a new method, one should at least to take into account the basic achievements in this field made earlier. Besides, the accuracy and reliability of a newly developed method should not be lower than that of already existing methods if their application require the same computational efforts. Therefore we consider the present ECAPP technique as a step in back direction as compared to the shape-consistent RECP version developed more than twenty years ago.

At last we should say that we did not find any serious scientific analysis of our conclusions and results in the Dolg’s paper but only some “political declarations” are there. Therefore, we are not going to answer in future on claims of similar quality as in the commented paper only because do not want to lose time on such a level of discussion as is proposed by Prof. Dolg. Any well-justified critical remarks concerning our GRECPs (or the text in our papers) are welcomed. We will answer with pleasure on questions dealing with RECPs. We are ready to (and welcome) any public discussion on the RECP methods (e.g., within the REHE newsletters) if they will be of common interest.

ACKNOWLEDGMENTS

We are grateful to M. Dolg for sending us the discussed paper that have stimulated us for writing these comments.

The work on development of the GRECP method was supported by the DFG/RFBR grant N 96–03–00069, the INTAS grant No 96–1266 and by the RFBR grant N 99–03–33249.
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Prof. Dolg twice refused to send us the parameters of his new ECPPs for Hg, at first, when we were preparing paper [11] (and therefore we were forced to use their previous PP version for Hg in our RECP comparison in [11]) and then, after publishing the results with the new ECPPs in the commented paper.

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TABLE I. The frozen core approximation (FCA) errors calculated by us with the help of the HFD \cite{22} code at the all-electron Dirac-Fock level within the point nuclear model for the states averaged over the nonrelativistic configurations. The errors of the new ECPP from Table 1 in the Dolg’s paper. All values are in cm$^{-1}$.

| configuration | FCA$^a$ | ECPP$^b$ |
|---------------|---------|----------|
| Hg $6s^2$     | 0.0     | 0.0      |
| Hg $6s^16p^1$ | 0.6     | 0.0      |
| Hg$^+$ $6s^1$ | 1.0     | 0.0      |
| Hg$^+$ $7s^1$ | 4.0     | 0.0      |
| Hg$^+$ $8s^1$ | 4.3     | 0.1      |
| Hg$^+$ $9s^1$ | 4.4     | -0.1     |
| Hg$^+$ $6p^1$ | 3.3     | 0.0      |
| Hg$^+$ $7p^1$ | 4.3     | 0.0      |
| Hg$^+$ $8p^1$ | 4.4     | 0.0      |
| Hg$^+$ $9p^1$ | 4.5     | 0.0      |

$^a$ frozen core approximation with the 1s, . . . , 4f frozen shells taken from the 6s$^2$ Hg state.  
$^b$ energy-consistent pseudopotential with 54 adjustable parameters.
APPENDIX A:

Because the reader can be not familiar with the criticized paper of Prof. Dolg, below we present its section 5.3, which is discussed in our comments, without any changes.

M. Dolg, Section 5.3 “Limitations of accuracy”

Effective core potentials are usually derived for atomic systems at the finite difference level and used in subsequent molecular calculations using finite basis sets. They are designated to model the more accurate all-electron calculations at low cost, but without significant loss of accuracy. Unfortunately the correct relativistic all-electron Hamiltonian for a many-electron system is not known and the various pseudopotentials merely model the existing approximate formulations. For most cases of chemical interest, e.g., geometries and binding energies, it usually does not matter which particular Hamiltonian model is used, i.e., typically errors due to the finite basis set expansion or the limited correlation treatment are much larger than the small differences between the various all-electron models.

Table 1. Relative average energy of a configuration of Hg from all-electron (AE) multi-configuration Dirac-Hartree-Fock (DHF) average level calculations using the Dirac-Coulomb (DC) Hamiltonian with a finite nucleus with Fermi charge distribution (fn) or a point nucleus (pn). Contributions from the frequency-dependent Breit (B) interaction (frequency of the exchanged photon 10^3 cm⁻¹) and estimated contributions from quantum electrodynamics (QED, i.e., self-interaction and vacuum polarization) were evaluated in first-order perturbation theory. Errors of energy-consistent pseudopotentials (PP) with 20 valence electrons and different numbers of adjustable parameters with respect to the AE DHF(DC,pn)+B+QED data. All values in cm⁻¹.

| configuration | AE, DHF (DC)+B+QED | contribution | error |
|---------------|---------------------|--------------|-------|
|               | fn                  |              |       |
| Hg            | 6s²                 | 0            | 0.0   | 0.0   |
|               | 6s¹6p¹              | 35632.3      | -52.5 | -18.7 | 1.3  |
| Hg+           | 6s¹                 | 68842.1      | -98.6 | -11.6 | -0.1 |
|               | 7s¹                 | 154127.4     | -220.6| -42.4 | -0.4 |
|               | 8s¹                 | 178127.5     | -238.4| -41.7 | 1.1  |
|               | 9s¹                 | 188751.0     | -244.1| -40.6 | 1.6  |
|               | 6p¹                 | 122036.8     | -154.2| -41.8 | 0.6  |
|               | 7p¹                 | 167514.3     | -224.1| -40.3 | -3.3 |
|               | 8p¹                 | 183808.0     | -238.5| -40.0 | -0.8 |
|               | 9p¹                 | 191697.2     | -244.0| -39.6 | 0.6  |
| Hg++          | 206962.2            | 207058.4     | -249.8| -39.5 | 2.6  |

*energy-consistent pseudopotential with 26 adjustable parameters.*

*energy-consistent pseudopotential with 54 adjustable parameters.*
For very accurate calculations of excitation energies, ionization potentials and electron affinities, or for a detailed investigation of errors inherent in the effective core potential approach, however, such differences might become important. Tables 1 and 2 demonstrate that for very special cases like Hg, with a closed 5d\textsuperscript{10}-shell in all electronic states considered, a small-core energy-consistent pseudopotential using a semilocal ansatz reaches an accuracy of 10 cm\textsuperscript{-1}, which is well below the effects of the nuclear model, the Breit interaction or higher-order quantum electrodynamical contributions. We also note that differences between results obtained with a frequency-dependent Breit term and the corresponding low-frequency limit amount to up to 10 cm\textsuperscript{-1}. Moreover, the quantum electrodynamic corrections listed in tables 1 and 2 might change by up to 20 cm\textsuperscript{-1} when more recent methods of their estimation are applied \cite{98,99}. Therefore, it is important to state exactly which relativistic all-electron model the effective core potential simulates and, when comparing effective core potentials of different origins, to separate differences in the underlying all-electron approach from errors in the potential itself, e.g., due to the size of the core, the method of adjustment or the form of the valence model Hamiltonian. In this context we want to point out that the seemingly large errors for energy-adjusted pseudopotentials reported by Mosyagin et al.\cite{100,101} are mainly due to the invalid comparison of Wood-Boring-energy-adjusted and Dirac-Fock-orbital-adjusted pseudopotentials to all-electron Dirac-Fock data, i.e., differences in the all-electron model are considered to be pseudopotential errors.

Note that in the above example of Hg the average energy of a configuration (table 1) and the fine-structure (table 2) of one-valence electron states is more accurately represented than the fine-structure of the 6s\textsuperscript{1}6p\textsuperscript{1} configuration. The small errors in the latter case are a consequence of the pseudoorbital transformation and the overestimation of the 6s-6p exchange integral with pseudo-valence spinors. This error could be reduced further upon using a smaller core, but the efficiency of the approach would be sacrificed. It is also obvious from the compiled data that the accuracy of the valence model Hamiltonian is also a question of the number of adjustable parameters. Claims that such very high accuracy as demonstrated here can only be achieved by adding nonlocal terms for outer core orbitals to the usual semilocal terms\cite{100,101} appear to be invalid, at least for energy-consistent pseudopotentials. Moreover, additional nonlocal terms obviously do not improve

\footnote{P. Pyykkö, M. Tokman, and L.N. Labzowski, Estimated valence-level Lamb shifts for group 1 and group 11 metal atoms, Phys. Rev. A \textbf{57}, R689 (1998).}

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the performance for atomic states with a 5d\textsuperscript{9} occupation or in molecular calculations (cf., e.g., tables III and XVII in Mosyagin et al.\textsuperscript{100}).

Table 2. As table 1, but for fine-structure splittings. All values in cm\textsuperscript{-1}.

| configuration | splitting       | AE,DHF (DC)+B+QED | contribution | error |
|---------------|-----------------|--------------------|--------------|-------|
|               |                 | fn                 | pn           | B     | QED   | PP\textsuperscript{a} | PP\textsuperscript{b} |
| Hg \(6s^16p^1\) | \(3^1P_1 - 3^3P_0\) | 1987.7             | 1988.6       | -25.5 | 0.9   | -14.7           | 3.0           |
|               | \(3^3P_3 - 3^3P_0\) | 6082.6             | 6084.8       | -96.8 | 2.9   | -28.3           | -3.5          |
|               | \(^1P_1 - 3^3P_0\) | 22994.4            | 22982.3      | -72.4 | 2.2   | -12.4           | -9.4          |
| Hg\textsuperscript{+} \(6p^1\) | \(^2P_{3/2} - ^2P_{1/2}\) | 7765.3             | 7768.8       | -132.8 | 4.8   | -14.8           | -0.1          |
|               | \(^2P_{3/2} - ^2P_{1/2}\) | 2136.8             | 2137.9       | -29.0  | 1.1   | -1.7            | 0.2           |
|               | \(^2P_{3/2} - ^2P_{1/2}\) | 939.4              | 939.9        | -12.1  | 0.4   | -4.6            | -0.3          |
|               | \(^2P_{3/2} - ^2P_{1/2}\) | 498.7              | 498.9        | -6.2   | 0.2   | -3.5            | 0.0           |

\textsuperscript{a} energy-consistent pseudopotential with 26 adjustable parameters.

\textsuperscript{b} energy-consistent pseudopotential with 54 adjustable parameters.