GRECP/5e-MRD-CI calculation of the electronic structure of PbH.

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Abstract. The correlation calculation of the electronic structure of PbH is carried out with the Generalized Relativistic Effective Core Potential (GRECP) and MultiReference single- and Double-excitation Configuration Interaction (MRD-CI) methods. The 22-electron GRECP for Pb is used and the outer core $5s$, $5p$ and $5d$ pseudospinors are frozen using the level-shift technique, so only five external electrons of PbH are correlated. A new configuration selection scheme with respect to the relativistic multireference states is employed in the framework of the MRD-CI method. The $[6,4,3,2]$ correlation spin-orbit basis set is optimized in the coupled cluster calculations on the Pb atom using a recently proposed procedure, in which functions in the spin-orbital basis set are generated from calculations of different ionic states of the Pb atom and those functions are considered optimal which provide the stationary point for some energy functional. Spectroscopic constants for the two lowest-lying electronic states of PbH ($^2\Pi_{1/2}, ^2\Pi_{3/2}$) are found to be in good agreement with the experimental data.

PACS numbers: 31.15.+q, 31.20.Di, 71.10.+x

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1. Introduction

The Relativistic Effective Core Potential (RECP) method has been widely used in recent years in the correlation calculations of molecules with heavy and super-heavy atoms (see e.g. [1]). This method allows one to treat explicitly only those electrons which play the most important role in the making of chemical bonds, while interactions with the core electrons and relativistic effects are described with the help of some effective one-electron operator (usually semi-local) in the Hamiltonian. Depending on the desired or reachable level of accuracy, one can choose an effective Hamiltonian which provides the minimal computational effort for the given accuracy. Accordingly, the accuracy of the method used for treating correlations and that of the RECP method should be consistent. From that point of view, the PbH molecule is of considerable interest as a testing system. In calculations on the Pb atom [2], a comparable level of accuracy for the Generalized RECP (GRECP) and correlation calculation methods was observed. PbH is a weakly bound system so the accuracy of the correlation calculation on the molecule can be expected to be close to the accuracy of the correlation calculation on the Pb atom.

The GRECP method [3] developed in PNPI allows one to attain a level of accuracy which is better than 200 cm$^{-1}$ for transition energies in correlation calculations of different heavy atoms and their ions [2, 4]. Our recent calculations [5] also show that the MRD-CI method with an improved selection scheme and properly chosen basis set enables one to reach a level of accuracy for molecular calculations involving heavy atoms which is comparable to the accuracy of the GRECP calculations for transition energies between electronic terms in those atoms.

It can also be noted that from valence CI calculations and subsequent calculations by the Relativistic Coupled Cluster method with Single and Double excitations (RCC-SD) with the same number of the correlated electrons, one can easily calculate contributions to the total energy from higher-order cluster amplitudes first of all in order to account for nondynamic correlation effects in the valence region. That information can be used in subsequent calculations by the RCC-SD method with an increased number of correlated electrons to give a significant improvement in the accuracy for the description of correlation structure of the system of interest [2].

2. Methods

A detailed description of the methods used in the present calculations can be found elsewhere [3, 4, 6]. Here we give only brief description and specifics of each method.

The GRECP operator contains non-local terms with the projectors on outer-core pseudospinors, together with the radially-local terms common for other RECPs. The addition of non-local terms is connected with a distinction between the effective potentials for outer-core and valence electrons. It should be noted that one-electron integral calculations with GRECPs are only slightly more time-consuming than with ordinary radially-local RECPs, but this time is negligible in comparison with the time
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needed for two-electron integral calculations.

In the MRD-CI method only those Spin (and Space Symmetry) Adapted Functions (SAFs) are included in the CI calculation which provide the values of the second-order perturbation theory corrections to the energy

$$\Delta E_I = \frac{|<\Phi_I|H|\Psi_0>|^2}{E_I - E_0} \quad (1)$$

which are greater than some threshold $T_0$. In the above equation, $\Psi_0$ is some multireference function and $\{\Phi_I\}$ are the trial SAFs. As, in particular, was shown in for systems with large Spin-Orbit (SO) interaction, it is preferable to choose $\Psi_0$ as an eigenvector of some Hamiltonian including SO terms. The perturbation corrections for the $T=0$ threshold to the total state energies are applied after the final SO-CI calculations and Davidson corrections are calculated for each term.

3. Basis set

To generate and optimize basis set for heavy atoms we mainly followed the procedure described in detail in. The main features of that procedure are:

1. A number of the trial one-electron basis functions is generated in Dirac-Fock or Hartree-Fock calculations of different ionic states of the atom of interest with the frozen core orbitals. In our case, two-component Hartree-Fock calculations with the spin-averaged part of the GRECP (Averaged GRECP or AGREP) were carried out. As a result, one-electron functions with the same $n$ and $l$ quantum numbers become degenerate. Core orbitals are obtained from the AGREP/SCF calculations of the Pb$^{2+}$ ion (5s,p,d and 6s orbitals in the case of a 22-electron GRECP). Then SCF calculations are performed with a different number of electrons in the frozen-core orbitals and an electron occupying some valence orbital (e.g. 6p).

2. The correlation calculation is performed with each generated function included in the basis set. We carried out RCC-SD calculations of five lowest-lying states of the Pb atom with the 6s$^2$ 6p$^2$ leading configuration (see for more computational details). In these calculations the $j$-dependent part of the GRECP (Effective Generalized Spin-Orbit Potential or EGSOP) is included in the effective Hamiltonian together with AGREP. Thus, effects caused by the SO interaction are taken into account on the basis set of many-electron spin-orbital functions. It is clear that for the adequate description of the correlation effects the number of stored nonidentical two-electron integrals on the spin-orbital basis set is substantially smaller than that on the spinor basis set. Therefore, calculations on the spin-orbital basis sets can be more efficient if correlation is more important than spin-orbit interaction as it usually takes place for valence electrons.

3. The value of some energy functional is calculated using the correlation energies obtained in the previous calculations. If the change of this functional (as compared to the value of the functional obtained in the previous step) for some function
is maximal in comparison with the cases of using other generated functions and exceeds a given threshold, that function is added to the correlation basis set. Otherwise, we neglect the function and the procedure starts from step 1 for an orbital with other \( n \) and \( l \) quantum numbers.

4. Results

We have carried out three series of MRD-CI calculations for the four states going to the two lowest dissociation limits of the PbH molecule. Five external electrons are correlated and the \( 5s_{1/2} \), \( 5p_{1/2,3/2} \) and \( 5d_{3/2,5/2} \) pseudospinors are frozen from the two-component GRECP/SCF calculation of the ground state of the \( \text{Pb}^{2+} \) ion (configuration \( 6s^2 \)). At the first run, a few of the lowest-energy configuration functions in irreducible representations of the nonrelativistic symmetry group were taken for each electronic term at each point of the potential curves as the initial approximation for \( \Psi_0 \) (i.e. reference configurations). For the next two runs, those configurations are chosen as the reference configurations which give the largest absolute values of CI coefficients, \( C_I \), at the previous run. The number of the reference configurations is selected using “CNFSORT” code \([8]\) such that their total contribution to the wavefunction (\( C^2_{\text{ref}} \equiv \sum_{I \in \text{ref}} C^2_I \)) is approximately equal to 96\% at the second run and to 98\% at the third run for each of the considered states and internuclear distances of the PbH molecule (for more details, see paper by Mosyagin et al. from the same volume and paper \([5]\)).

As “MRD-CI” program package only allows the use of symmetry group \( D_{2h} \) and lower orders, all calculations have been performed in the relativistic double group symmetry \( C_{2v} \). Molecular spin-orbitals are obtained from SCF calculations performed by program module “SCF” in “MOLCAS” package \([10]\). The correlation spin-orbital basis set for Pb \([6,4,3,2]\) generated in the way described above and basis set from \([11]\) reduced to \([3,2,1]\) for H are used. We estimate Basis Set Superposition Error (BSSE) by calculating the Pb atom in the molecular basis set, i.e. with “ghost” H atom at different distances. In our calculations the BSSE does not exceed 70 cm\(^{-1}\). The following formula is used for the \( T=0 \) energy correction:

\[
E_{T=0} \simeq E_{T=T_k} - \lambda \sum_{\Delta E_I < T_k} \Delta E_I ,
\]

where \( E_{T=T_k} \) and \( E_{T=0} \) are the total state energies calculated for the \( T_k \) and zero thresholds, \( \Delta E_I \) is the energy lowering for the unselected SAFs estimated by equation \((1)\). The \( \lambda \) constant is determined from calculations with two different thresholds, \( T_1 \) and \( T_2 \):

\[
E_{T=T_1} - \lambda \sum_{\Delta E_I < T_1} \Delta E_I = E_{T=T_2} - \lambda \sum_{\Delta E_I < T_2} \Delta E_I .
\]

When applying the perturbation energy correction, the value of \( \lambda \) never exceeds 3 with the thresholds from 0.5\( \mu H \) to 0.03\( \mu H \). Potential curves for the four lowest-lying electronic states are presented on Figure 1. Molecular spectroscopic constants were
calculated by the Dunham method in the Born-Oppenheimer approximation using the DUNHAM-SPECTR code [9].

Spectroscopic constants for the two lowest-lying molecular electronic terms are given in Table 1. The next two electronic levels cannot be characterized in the same way, as can be seen from Figure 1.

Acknowledgments

This work was supported by DFG/RFBR grant No 96–03–00069. T I, N M and A T also thank RFBR grants No 01–03–06334, 01–03–06335, and 99–03–33249. Essential part of the present calculations was carried out in the computer center of the Bergische Universität Wuppertal.

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Table 1. Spectroscopical constants ($R_e$ — bond length, $D_0$ — dissociation energy, $\omega_e$ — vibrational constant, $T_e$ — transition energy) for the ground and first excited states of PbH.

| Term   | Calculated | Experimental |
|--------|------------|--------------|
| $^2\Sigma_{1/2}$ | $R_e = 1.871$ Å | $R_e = 1.838$ Å |
|        | $\omega_e = 1686cm^{-1}$ | $\omega_e = 1564cm^{-1}$ |
|        | $D_0 = 1.44eV$ | $D_0 \leq 1.59eV$ |
| $^2\Pi_{3/2}$ | $R_e = 1.855$ Å | |
|        | $\omega_e = 1727cm^{-1}$ | |
|        | $T_e = 6427cm^{-1}$ | $T_e \sim 6900cm^{-1}$ a) |

a) Unpublished data by Fink et al.

The potential curves from GRECP/5e-MRD-CI calculations of PbH. Intermolecular distance (X-axis) and total valence energy (Y-axis) are in a.u.