http://dx.doi.org/10.5012/bkcs.2012.33.3.803

Two-Component Spin-orbit Effective Core Potential Calculations with an All-electron Relativistic Program DIRAC†

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Received November 15, 2011, Accepted December 13, 2011

We have implemented two-component spin-orbit relativistic effective core potential (SOREP) methods in an all-electron relativistic program DIRAC. This extends the capacity of the two-component SOREP method to many ground and excited state calculations in a single program. As the test cases, geometries and energies of the small halogen molecules were studied. Several two-component methods are compared by using spin-orbit and scalar relativistic effective core potentials. For the I_2 molecule, excitation energies of low-lying excited states agree well with those from corresponding all-electron methods. Efficiencies in SOREP calculations enhanced by using symmetries are also discussed briefly.

Key Words : Two-component method, Relativistic effective core potentials, Spin-orbit interaction, Hydrogen Halide, Hydrogen bihalide

Introduction

Understanding of chemical systems including heavy elements has been rapidly growing in recent years.[1,2] Not only academic areas but realms in industry, heavy elements play crucial role at present. However, describing heavy element in quantum mechanical calculation has practical barriers from the complexities in the calculation. As the elements become heavier, the nonrelativistic Schrödinger equation often fails to describe the electronic structures properly. For a reliable description of many molecules containing heavy elements, one should apply the methods based on the relativistic Dirac equation. However, the straightforward application of the Dirac equation is still quite limited due to the computational complexity. For this reason, many modified and simplified approximations to Dirac equations have been proposed.[3] Among them, relativistic effective core potential (RECP)[4] has been one of the most popular approximations since RECP can include two important relativistic effects. The scalar relativistic effect – mainly comes from mass-velocity and Darwin terms – is incorporated into the average relativistic effective core potential (AREP). When the spin-orbit terms, which are remaining important relativistic effects, are added to AREP, the spin-orbit relativistic effective core potential (SOREP) is obtained. One of main advantages of using RECP is that spin-orbit terms can be considered at various stages of calculations. By choosing AREP or SOREP, the spin-orbit effect can be excluded or included in the RECP calculations, respectively.

Many variations of AREP can be readily implemented in conventional general quantum mechanical programs since the effective Hamiltonian for AREP is same in form to non-relativistic Hamiltonian (Sec. II-A). SOREP, however, needs more complicated 2-component Hamiltonian, and several programs utilizing SOREP have been proposed from our group[5-10] and others.[4] However, those few programs supporting SOREP calculations have quite limited capabilities limited in specific theories for each program.

In this paper, we report the implementation of an RECP method in a general purpose relativistic program DIRAC.[11] For the ground state calculation, several theories including Hatree-Fock (HF), density functional theory (DFT), Moller-Plesset second order perturbation (MP2), configuration interaction (CI), coupled-cluster (CC), and Fock-space coupled cluster (FSCC)[4] can be used in both the AREP and the SOREP method. Excited state calculations are also allowed through CI and FSCC theories. From the comparison of several correlated methods, we will show that RECP is easily applicable to ground and excited states of several systems which have noticeable relativistic effects. The comparison can also be made with other relativistic Hamiltonians. In the following section, efficiencies expected in practical calculation were tested through the adaption of several symmetries. In the current version of DIRAC, eight symmetries from C_1 to D_{2h} are allowed in the RECP calculation. As test cases, several halogen molecular systems, HX and XHX^- (X=Cl, Br, I) were calculated. Vertical Excitation energies of I_2 were also compared with other all-electron methods.

Theory

Relativistic Effective Core Potential Model. One of the earliest version of SOREP or two-component RECPs were derived by Lee *et al.*[12] from the modification of semi-local form of pseudo-potential.[13,14] Resulting two-component effective Hamiltonian for n_v-valence electron is expressed as,

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† This paper is to commemorate Professor Kook Joe Shin's honourable retirement.

$$\hat{H} = \sum_{i=1}^{n_v} \hat{h}_i + \sum_{i<j}^{n_v} \hat{g}_{ij} \tag{1}$$

$$h_i = -\frac{1}{2}\nabla_i^2 + \sum_{a=1}^{n_v}\left(-\frac{Z_a^{eff}}{r_{ai}} + U_a^{RECP}\right) \tag{2}$$

where i and j denote elections, Z_a^{eff} is the effective charge for valence elections, a is core indices, and U_a^{RECP} indicates RECP of atom a.

The RECP can be described in many ways depending on the description of the spin-orbit part. Here, we classify RECP as SOREP and AREP. As in the original paper,[12] spin dependent term is included in SOREP to have a general expansion form as,

$$U^{SOREP} = \sum_{l=0}^{\infty} \sum_{j=|l-1/2|}^{l+1/2} \sum_{m=-j}^{j} U_{lj}^{SOREP}(r)|ljm\rangle\langle ljm| \,. \tag{3}$$

Since all potential terms including relativistic effects become similar for highly excited orbitals of higher angular momenta, the infinite expansion can be approximated as,

$$U^{SOREP} \approx U_{LJ}^{SOREP}(r) + \sum_{l=0}^{L-1} \sum_{j=|l-1/2|}^{l+1/2} \sum_{m=-j}^{j} [U_{lj}^{SOREP}(r) - U_{LJ}^{SOREP}(r)]|ljm\rangle\langle lim| \,. \tag{4}$$

From the above spin-dependent expression of RECP, Ermler *et al.*[15] proposed a modified form by introducing effective one-electron spin-orbit (ESO) operator. From the definition of ESO, SOREP (U^{SOREP}) can be divided into two types of a potential – AREP (U^{AREP}) and spin-orbit potential (U^{SO}) – from the separation of spin-orbit part in the potential.

$$U^{SOREP} = U^{AREP} + U^{SO} \tag{5}$$

In Eq. (5), U^{AREP} has the form,

$$U^{AREP} = U_L^{AREP}(r) + \sum_{l=0}^{L-1} \sum_{m=-l}^{l} [U_l^{AREP}(r) - U_L^{AREP}(r)]|lm\rangle\langle lm| \;, \tag{6}$$

where

$$U_l^{AREP}(r) = \frac{1}{2l+1}[l \cdot U_{l,l-1/2}^{SOREP}(r) + (l+1) \cdot U_{l,l+1/2}^{SOREP}(r)] \,. \tag{7}$$

The spin-orbit potential (U^{SO}) is defined as,

$$U^{SO} = s \cdot \sum_{l=1}^{L} \frac{2}{2l+1} \Delta U_l^{SOREP}(r) \sum_{m=-l}^{l} \sum_{m'=-l}^{l} |ljm\rangle\langle lim|l|lm'\rangle\langle lm'| \tag{8}$$

with

$$\Delta U_l^{SOREP}(r) = U_{l,l+1/2}^{SOREP}(r) - U_{l,l-1/2}^{SOREP}(r) \,. \tag{9}$$

Advantage from this form of definition is that one can neglect spin-orbit coupling term by employing only the potential U^{AREP} and omitting U^{SO} part. Thus, the scalar relativistic effect and the spin-orbit effect are easily separated and treated at different levels. With U^{SO}, radial functions of the two atomic spinors with $j = l + 1/2$ and $j = l-1/2$ become different when SOREP is used to generated one electron wave function. Omitting U^{SO}, amounts to using average of two spinors of same l but differing in j as the l orbital. This AREP method is entirely the same in form as nonrelativistic effective core potential methods. AREP calculations can be performed with nonrelativistic quantum chemistry programs once the AREP integrals over basis sets are available. One can do two-component SOREP calculations when both AREP and ESO are included, but this requires programs to handle two component spinors. The present work is an effort to use an all-electron relativistic program DIRAC for this purpose. In the quantum chemical applications the radial part of RECP is expressed as an expansion of analytic functions, usually Gaussians. Then any effective core potentials having the form given above can be utilized in the program. Two types of RECPs most relevant to the present presentation are – the shape-consistence (SC) and the energy-adjusted (EA) RECPs that are based on nodeless pseudo-orbitals.[4]

Implementation. In this section, an implementation of one-electron RECP integrals will be discussed briefly. The schematic view of implementation is shown in Figure 1.

In Figure 1, a simplified description of the main program routines in DIRAC is shown. The names with and without box in the figure indicate names of subroutines and files used in modified DIRAC program, respectively. When the DIRAC program[11] starts, the input module (PAMNP) reads an original input and sets up symmetric information including transformation matrices from atomic orbitals to symmetry orbitals. From these, the INPUT file of the RECPINT program is generated. The main RECPINT routine (based on ARGOS integral routine[16]) is called after the DIRAC input module, and calculate nuclear attraction integrals and spin-orbit integrals. AREP parameters go into the potential in Eq. (6) and SO parameters are defined in Eq. (8). When the RECPINT routine is completed, VCORE, SOX, SOY, and SOZ files are extracted. First file (VCORE) is from the nuclear attraction integral. Three remaining files (SOX, SOY, and SOZ) are from spin-orbit integrals, treated like x, y, and z components of Pauli matrices in the Dirac equation. Thus, in the case of the AREP calculation, elements of these three matrices related to spin-orbit integrals will be zero. They are placed as effective potential (U^{RECP}) in one-electron operator, Eq. (2). Reading files from the RECPINT routine is performed by the PAMSET routine. After setting all integrals needed, self-consistent-field (SCF) iteration module (PAMDRV) works. Further electron correlation calculations can be obtained from the molecular spinors obtained after the SCF iteration. We use spinors to express one electron wave functions for which α spin-orbitals and β spin-orbitals mix to form two-component or four-component functions.

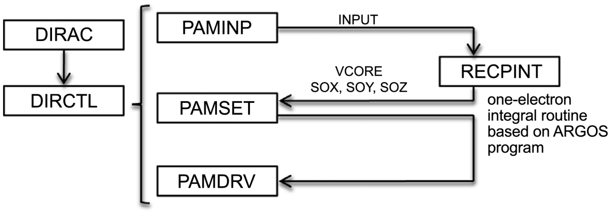

Figure 1. Schematic view of interfacing RECP integrals in the DIRAC package.

Efficiencies with Symmetry. Exploitation of the spatial symmetry is one advantage of the present implementation. In the effective molecular Hamiltonian, the one-electron part is modified by RECP (U^{RECP}, Eq. 2). As shown in section B, nuclear attraction integrals (V) and SOREP integrals (σ_x, σ_y, σ_z) are calculated in the RECPINT routine. Other integrals such as overlap and kinetic (T) integrals are obtained from the routine in the DIRAC program. AREPs are placed in diagonal parts of symmetry blocks in the one-electron Fock-matrix whereas SOREPs go to off-diagonal parts. Each one and two-electron Fock matrix can be divided into symmetry blocks in DIRAC. For example, the one-electron Fock matrix (F^1) for the C_{2V} symmetry is following,

$$F^1 = \begin{bmatrix} T+V & \sigma_Z & \sigma_Y & \sigma_X \\ \sigma_Z & T+V & \sigma_X & \sigma_Y \\ \sigma_Y & \sigma_X & T+V & \sigma_Z \\ \sigma_X & \sigma_Y & \sigma_Z & T+V \end{bmatrix} \qquad (10)$$

where each column and row indicates A1, A2, B1, and B2 irrep., respectively. An example form of the F matrix is presented here to show that different symmetry blocks are connected by spin-orbit terms in the SOREP-KRHF method.

In Table 1, the results from C_1 to D_{2h} symmetry are listed for the test case of tetrachloro ethylene (C_2Cl_4) molecule obtained in Kramer Restricted Hartree-Fock (KRHF) calculations. For the carbon atom, aug-cc-pVTZ basis set[17,18] was used. Christiansen 7 valence SOREP[19] with the modified basis set of Lee *et al*.[20] was used for the Chlorine atom. The f functions of atomic basis sets were neglected in Table 1 for the convenience. Test calculations were performed using an AMD Athlon(TM) 64 X2 Dual Core Processor 4600+. Only single CPU was used in this task.

First, as seen from C_1 to D_{2h}, the time decreases by adapting symmetry. The C_1 symmetry case took 392 seconds. Whereas in the C_s symmetry, elapsed time was 232 seconds (less than two thirds of the C_1 case). The D_{2h} symmetry took only 152 seconds which is almost one third of the C_1 symmetry. The total computation time provides only the partial information, but clearly demonstrated is the reduction of time with symmetries. When the size of the system is bigger, more time saving from the applying symmetry will be observed.

Another important issue in a practical calculation is the disk usage which is also compared in Table 1. Three files are compared and all of them show larger reductions than the CPU times. The VCORE files have the information of nuclear interaction integral. They were generated from RECPINT routine with several symmetries, and copied to DIRAC program. As they have more symmetry, larger savings occur. The DFCOEF file contains MO expansion coefficients from the SCF iteration, and DFFCK1 is the one electron Fock matrix file. These files are formed in the SCF calculation after reading integral files. For example, DFCOEF file for the C_1 symmetry is 1,241,682 byte. With the C_S symmetry, the size is reduced to almost half. When the D_{2h} symmetry is adapted, the files are decreased to 157,310 which is approximately one tenth of the size in the C_1. Compared to CPU time, more substantial savings are realized in the use of disk resource.

Table 1. Time and disk usage in C_2Cl_4 calculation

	File	C_1	C_s	D_{2h}
Computational time (sec)		392	232	152
Disk usage (byte)	VCORE	170,576	85,740	26,296
	DFCOEF	1,241,682	622,034	157,310
	DFFCK1	1,358,058	679,082	339,594

*See text for the computation details

Test Calculations

Hydrogen Halide (HX) and Hydrogen Bihalide Anion (XHX^-). In this section, RECP calculations of hydrogen halide (HX) and hydrogen bihalide anion (XHX^-) molecules are compared for several methods. First, we studied hydrogen halides which are well-known molecules both in theories[21] and experiments.[22] The XHX^- molecules are relatively unknown in experiments.[23,24] Several methods from RECP will also be compared with all-electron (AE) calculations for the reliabilities.

The methods used here are HF, MP2, DFT, CC theories for AREP, and their spin-orbit two-component counterparts, Kreamer-restricted HF (KRHF), KR-MP2, KR-DFT, KR-CC, respectively, for SOREP. Three different perturbative triples contributions in CCSD theory (CCSD+T, CCSD(T) and CCSD-T)[25] were also obtained. AREP and SOREP used in this calculation were shape-consistent RECPs generated by Christiansen *et al.* with 7 valence electrons.[19] Basis sets for these ECP are (7s7p3d2f)/[4s4p3d2f] which were optimized by Lee *et al.*.[20] For comparisons with RECP calculation, all-electron Dirac-Hartree-Fock (DHF)[3] calculations were also conducted. All-electron basis-sets are from Dunning's cc-pVTZ basis-set[17,18] for chlorine and Dyall's pVTZ basis-set[26] for bromine and iodine. In the case of the hydrogen, Aug-cc-pVTZ basis set[17,18] was used for all calculations. All calculations were conducted from the newly modified-DIRAC program.

In Table 2, bonding distances of hydrogen halide (HX) and hydrogen bihalide (XHX^-) molecules are listed for several methods. Geometries in each type of molecules follow similar tendencies among different theories. For the HX molecules, dynamic correlation elongates bond lengths, whereas those in XHX^- molecules appear in opposite directions except for the B3LYP[27] method. The B3LYP method is very close to CCSD in both AREP and SOREP for HX, but differs significantly from other correlation methods in XHX^- molecules. B3LYP tends to overestimate bond lengths compared to CCSD(T) in both HX and XHX^-, whereas the MP2 calculation had the bond length 0.01 Å shorter than CCSD(T). Effects of triple excitations in coupled cluster theory are similar in both HX and XHX^-. Changes from each triple correction are negligible, being less than 0.001 Å.

Compared with all-electron calculations, RECP calculations for HX molecules have shorter bond lengths. But the

Table 2. Equilibrium bond length R_e(in Å) of XHX^- molecules (X=Cl, Br, I)

Methods	HCl	HBr	HI	$ClHCl^-$	$BrHBr^-$	IHI^-
AREP-HF	1.263	1.402	1.596	1.564	1.712	1.927
SOREP-KRHF	1.263	1.402	1.598	1.564	1.712	1.929
AREP-B3LYP	1.282	1.420	1.611	1.576	1.723	1.934
SOREP- B3LYP	1.282	1.420	1.614	1.576	1.724	1.937
AREP-MP2	1.269	1.407	1.599	1.547	1.693	1.900
SOREP-KRMP2	1.269	1.408	1.602	1.547	1.693	1.902
AREP-CCSD	1.272	1.412	1.607	1.552	1.700	1.910
SOREP-KRCCSD	1.272	1.412	1.609	1.552	1.700	1.912
AREP-CCSD+T	1.274	1.414	1.609	1.553	1.702	1.911
SOREP-KRCCSD+T	1.274	1.415	1.612	1.553	1.702	1.913
AREP-CCSD(T)	1.274	1.414	1.609	1.553	1.701	1.911
SOREP-KRCCSD(T)	1.274	1.414	1.612	1.553	1.702	1.913
AREP-CCSD-T	1.274	1.414	1.609	1.553	1.701	1.911
SOREP-KRCCSD-T	1.274	1.414	1.612	1.553	1.702	1.913
DC-DHF	1.267[b]	1.406[b]	1.603[b]	1.567	1.722	1.932
DC-CCSD(T)	1.279[b]	1.419[b]	1.620[b]	-	-	-
Exp.	1.275[c]	1.414[c]	1.609[c]	1.573[d]		

[a] All numbers without superscript are obtained from modified version of DIRAC. See Section III-A. [b] Reference 21. [c] Reference 22. [d] Reference 23.

differences are not significant. SOREP-KRHF and all-electron (AE), DC-HF differ by 0.003-0.004 Å. The differences are similar in the case of CCSD(T). The difference in all-electron calculation of HX increase to 0.008 Å, but the others differ by 0.005 Å. Same tendencies are shown in XHX^- molecules. Spin-orbit effects for HX and XHX^- are negligible for HCl and $ClHCl^-$, but they increase as halogen atoms become heavier. For the HI and IHI^- molecules, these effects are as large as those of triple excitations.

When halogen ion (X^-) bond to HX molecules, to form XHX^-, bond elongations in HX appear. Most theories estimate that bond distances between H and X molecules become 0.3 ± 0.02 Å longer in XHX^- molecules. The trends of extension are similar in each theory. The changes of bond lengths between HBr and $BrHBr^-$ become about 0.01 Å larger than the ones of HCl and $ClHCl^-$. For the cases of the iodine, bond length changes are approximately 0.02 Å larger than bromine cases. The XHX^- system of heavy halogen elements is bonded less tightly, and this leads to smaller dissociation energies in Table 3. In all cases, largest bond changes occur at the HF level of theory. Discrepancies from CCSD(T) are 0.03 Å in iodine cases. The mean-field approximation is not quite suitable for the description of XHX^- system. KRCCSD(T) bond length differences are 0.279 Å, 0.288 Å, and 0.301 Å for Cl, Br, and I, respectively. Spin-orbit effects are rather small in the cases of elongation.

Dissociation energies of XHX^- are shown in Table 3. The energies are obtained from the energy differences between the stable XHX^- molecules and their dissociated products HX and X^-. The heavier the halogens, the smaller the dissociation energies. The KRCCSD(T) bonding energy of IHI^- is 86% of $BrHBr^-$ and 75% of $ClHCl^-$, which is in line with dissociation energies of HX molecules. The HF level of theory yields less than half of the dissociation energies. For the proper description of XHX^-, dynamic correlation effect seems crucial even though the assumed dissociation fragments are all closed-shell configurations. Results from the MP2 theory overestimate about 0.1 eV over the CCSD with triple correction values. The CCSD values show different trends from MP2 ones, underestimating by around 0.1 eV. Three different triple excitation treatments in coupled cluster approach have only minor effects. B3LYP results are relatively similar to the values from CCSD with triples. Spin-orbit effects are not significant in dissociation of XHX^-. Maximum differences obtained in the case of B3LYP describing heavier IHI^- molecule is only 0.003 eV. The small

Table 3. Dissociation energies (in eV) of XHX^- molecules (X=Cl, Br, I)

Methods	$ClHCl^-$	$BrHBr^-$	IHI^-
AREP-HF	0.646	0.492	0.269
SOREP-KRHF	0.646	0.491	0.269
AREP-B3LYP	1.033	0.913	0.737
SOREP-KRB3LYP	1.033	0.912	0.740
AREP-MP2	1.123	0.998	0.879
SOREP-KRMP2	1.123	0.997	0.882
AREP-CCSD	0.969	0.839	0.689
SOREP-KRCCSD	0.969	0.838	0.690
AREP-CCSD+T	1.043	0.918	0.785
SOREP-KRCCSD+T	1.043	0.917	0.787
AREP-CCSD(T)	1.043	0.917	0.784
SOREP-KRCCSD(T)	1.043	0.916	0.786
AREP-CCSD-T	1.042	0.916	0.783
SOREP-KRCCSD-T	1.042	0.915	0.785
Exp.	1.0[b]		

[a] All numbers are obtained from modified version of DIRAC. See Section III-A. [b] Reference 24.

Table 4. R_e(Å) and D_e(eV) of I_2 molecule from FSCCSD and CCSD(T) calculations

	$I_2(\sigma_g^2\pi_u^4\pi_g^4)^1\Sigma_{g,}^+$	
	R_e	D_e
AREP-FSCCSD[a]	2.678	1.73
SOREP-FSCCSD[a]	2.692	1.28
DC-FSCCSD[b]	2.691	1.47
DC-FSCCSD+BSSE[b]	2.711	1.32
DC-CCSD(T)[c]	2.668	1.57
Exp.[d]	2.666	1.55

[a]Present calculation, see Section III-B. [b]Reference 28. [c]Reference 29. [d]Reference 22.

spin-orbit difference is due to the closed shell configuration of HX and X^-. XHX^- can be used to understand XHX for which large spin-orbit effects are anticipated. When next extension of the DIRAC program makes this comparison possible, XHX^- will be studied in more detail along with XHX.

I_2 Molecule. Relativistic Fock-space coupled-cluster (FSCC)[4] for the two-component SOREP methods, which becomes available through the current modification, can be used to calculate transition energies including electron affinity (EA), ionization potential (IP), and excitation energies with high accuracy. Here, SOREP spinor based FSCC with single and double excitation (FSCCSD) is tested for the ground state of the I_2 molecule, and selected excitation energies for the same molecule are calculated using CI methods.

In Table 4, the equilibrium bond length and the dissociation energy of I_2 molecule are compared with other FSCCSD and DC-CCSD(T) methods. The comparison of SOREP-FSCCSD with all-electron DC-FSCCSD calculations[28] indicate that SOREP-FSCCSD yields bond lengths similar, but the dissociation energy is lower by 0.19 eV. The energy changes due to difference in basis set are expected to be large as can be seen from the comparison of DC-FSCCSD and DC-FSCCSD+BSSE. DC-CCSD(T) values[29] imply that the contribution from triple excitations will be also important to estimate experiment result.

Vertical excitation energies for the neutral I_2 molecule were examined using the general open shell CI (COSCI) routine[30] in the modified DIRAC program. COSCI does full CI calculation for the orbital (spinor) space specified. Orbitals (spinors) are generated from the average-of-configurations HF (KRHF). 6 molecular spinors are included in the CI space. Ground state of I_2 molecule has $\sigma_g^2\pi_u^4\pi_g^4\sigma_u^0$ configuration. Each excited configuration has dominant configuration $\sigma_g^k\pi_u^l\pi_g^m\sigma_u^n$ with k + l + m + n=10. Low lying excited states of the I_2 molecule were compared with other all-electron methods in Table 5. The results from SOREP spinor based COSCI (SOREP-COSCI) are very close to all-electron COSCI (AE-COSCI). All vertical energy differences with AE-COSCI are within 0.03 eV. Here, low-lying excited states are not affected seriously by the RECP approximation. When compared with more accurate MR-CISD results, many of SOREP-COSCI values are even closer to MR-CISD ones than AE-COSCI. Differences from experiment values[22,31,32] are significant, implying the necessity of larger CI space and one-electron basis sets.

Table 5. Vertical excitation energies of I_2 molecules.

ω-ω states[a]	Dominant configurations	SOREP-COSCI[b]	AE-COSCI[c]	MR-CISD[c]	Exp[d]
(1) 0_g^+	2440	0.00	0.00	0.00	0.00
(1) 2_u	2431	1.75	1.78	1.75	1.69
(1) 1_u	2431	1.92	1.95	1.91	1.84
(1) 0_u^-	2431	2.31	2.34	2.30	2.13
(1) 0_u^+	2431	2.47	2.50	2.43	2.37
(2) 1_u	2431	2.71	2.72	2.62	2.49
(1) 2_g	2341	3.60	3.62	3.59	
(1) 1_g	2341	3.69	3.71	3.69	
(2) 0_g^+	2341	4.18	4.21	4.17	
(1) 0_g^-	2341	4.32	4.34	4.25	
(2) 1_g	2341	4.49	4.49	4.41	
(2) 0_u^-	1441	4.65	4.64	4.64	
(3) 1_u	1441	4.72	4.71	4.67	4.57
(3) 0_g^+	2422	4.34	4.36	4.29	
(3) 1_g	2422	4.81	4.84	4.71	
(2) 2_g	2422	5.05	5.07	4.98	
(4) 0_g^+	2422, 2242[b]	5.77	5.79	5.64	
(3) 0_u^-	2332	4.99	5.02	5.10	
(1) 3_u	2332	4.97	5.00	5.11	
(2) 2_u	2332	5.67	5.66	5.73	

[a]Ordering of the states are followed the reference 29. [b]Present calculation, see Section III-B. [c]Reference 29. [d]Reference 22, 31, 32.

Conclusion

Two-component SOREP calculations were applied in HF and several correlated methods *via* modified DIRAC program. The program also exploits several Abelian group symmetries up to D_{2h}. Symmetry use reduces computational demands significantly at the HF step and beyond. Test calculations were conducted for several group 17 molecules, demonstrating that most of popular methods can be employed to estimate spin-orbit effects by comparing AREP and SOREP calculations of a given method. Excited states were also explored with RECP demonstrating that SOREP values are reasonably close to all-electron ones. We believe that the present implementation of SOREP in the DIRAC program could be of use to investigate relativistic effects on molecular systems which are difficult to treat at the all-electron level.

Acknowledgments. The authors thank Professors. Saue and Visscher for allowing us to modify the DIRAC program, and Prof. Pitzer for the ARGOS program. This work was supported by grants (2010-0016243, 2011-0001213) from National Research Foundation. Some of computational resources were provided by KISTI (KSC-2011-C2-18).

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