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Semiempirical Studies of Inner-Core Energy Levels. Part 7. ESCA Shifts of Germanium in Molecular Systems

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Shifts of the $3p_{2/3}$ energy levels of germanium in different chemical moieties were studied by using the semiempirical SCC-MO method. The calculations were performed within the framework of the electrostatic potential method in the point-charge approximation. Relaxation energies were explicitly taken into account by employing the equivalent core and transition potential methods. It was found out that the relaxation energy plays a decisive role in determining shifts along the series $GeH_4 \rightarrow Ge(CH_3)_4$. The results obtained by the equivalent core and transition potential methods are similar being in the same time in good agreement with experiment. Performance of various semiempirical schemes in evaluating ESCA shifts is briefly discussed.

X-ray photoelectron spectroscopy proved to be a useful tool in studying molecular properties in gas[1], liquid[2] and solid phase[3]. It is also a convenient technique for discussing bonding features in polymers[4] chemisorption and physisorption phenomena[5,6], homogenous catalysis[7] etc. An a priori treatment of the photoionization process is rather complicated because it includes Δ SCF calculation for each ionized atom in a molecule with explicit consideration of the relativistic and correlation effects. Consequently, it is feasible for small molecules. We have shown in a series of papers[8] that the self-consistent charge molecular orbital (SCC-MO) method in conjunction with simple electrostatic potential successfully accounts for the changes in core energy levels for the first and second row atoms. Additional advantage of this approach is its ease and wide applicability to large compounds of biochemical interest[9]. It is the aim of this work to show that the method can be extended to heavy atoms possessing large number of electrons. In particular, we discuss here ESCA shifts of germanium $3p_{3/2}$ levels in different chemical environments. All studied molecules are in vapour state.

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Our approach is well documented by now[10]. Briefly, ESCA chemical shifts are related to ground state gross valence electrons atomic charges via the equation

$$\Delta BE_A = k_1 Q_A + k_3 \sum_B{}' (Z_B - 2 - Q_B)/R_{AB} + k_4 \quad (1)$$

where the ionized atom is deliberately denoted by A and the sum goes over all other atoms B $\neq$ A. The adjustable empirical parameters are found by fitting the experimental innner-shell energy shifts employing the least-squares method. The second term in eq(1) is called Madelung energy and it will be abbreviated hereafter as M. By switching on and off the weighting factor k_3 we can examine the importance of M which, in turn, explicitly involves the structural characteristics of the studied molecule. The corresponding models using the sets of parameters (k_1, $k_3 = 0$, k_4) and (k_1, $k_3 \neq 0$, k_4) are denoted by Q and $Q + M$, respectively. Since in eq(1) is taken into account only the initial state this approach is termed ground state potential model (GPM). The energy of the relaxation process accompanying photoionization is to some extent absorbed in the weighting factors k_i (i = 1, 3, 4). The GPM method is sufficient for first row atoms with very few exceptions[8]. However, the effect of the final (ionic) state can be explicitly taken into account by using the transition potential[10] or equivalent core[11] methods. The transition potential formalism is based on the idea that both initial and final states could be incorporated in the transition operator. This procedure retains an appealing feature of the Koopman's theorem that only one calculation per atom is needed because the reorganization energy is implicitly included in transition operator's eigenvalues. The ESCA shifts are then given in the point-charge electrostatic potential approximation by

$$\Delta BE_A (t) = k_1 (t) Q_A^* (t) + k_3 (t) \sum_B{}' (Z_B - 2 - Q_B (t))/R_{AB} + k_4 (t) \quad (2)$$

where the gross valence electrons charges refer to a molecule possessing a pseudoatom A*. Its atomic parameters are arithmetic means of the values corresponding to atoms with nuclear charges Z_A and $Z_A + 1$.

According to the equivalent core concept valence electrons adjust upon the ejection of a core electron as if the nuclear charge of the ionized atom would be increased by a unit and the inner-shell is completed by an additional electron. The resulting electrostatic potential formula is of the form

$$\Delta BE_A (\text{e.c.}) = k_1 (\text{e.c.}) [\xi_A Q_A + \xi_{A+1} Q_A (\text{e.c.})] + $$
$$+ k_3 (\text{e.c.}) [M_A + M_{A+1} (\text{e.c.})] + k_4 (\text{e.c.}) \quad (3)$$

where ξ_A is Slater effective nuclear charge $Z_A - S_A$ and S_A is a screening constant. It arises due to the one-center integrals of the $1/r$ operator. The entities Q_A (e. c.) and M_{A+1} (e. c.) are obtained for the equivalent core calculation which is executed for the ground state molecular geometry. It is tacitly assumed here that nuclei are too inert to follow the relaxation of the electronic cloud. This is in most cases justified.

The experimental ESCA shifts for germanium are not very abundant[12]. The calculated values for seven different molecules obtained by using eqs(1—3)

TABLE I

Comparison Between the Calculated ESCA Shifts of Germanium $3p_{3/2}$ Levels as Obtained by the SCC-MO Ground State Potential, Transition Potential and Equivalent Cores Approaches and the Corresponding Experimental Data[a]

Molecule	Q^{GP}	$(Q+M)^{GP}$	Q^{TP}	$(Q+M)^{TP}$	$(Q+M)^{EC}$	Exp.
GeH_4	—1.0	—1.0	—1.1	—1.8	—1.8	—1.29
GeH_3CH_3	—1.4	—1.4	—1.1	—1.0	—1.1	—0.88
$Ge(CH_3)_4$	—2.3	—2.4	—1.1	0.1	0.0	0
GeF_4	—5.6	—5.6	—5.9	—5.9	—5.9	—5.71
GeH_3Cl	—1.6	—1.6	—1.5	—2.5	—2.5	—2.19
$GeCl_4$	—2.8	—2.8	—4.0	—3.4	—3.3	—4.08
GeH_3Br	—1.3	—1.3	—1.2	—1.7	—1.7	—2.0
			standard deviations			
present results	1.2	1.2	0.6	0.4	0.4	
EHT[a]		1.2			1.0	
CNDO/2[a]		0.5			0.5	

[a] Experimental data are taken from ref. 12.

and SCC-MO semiempirical wavefunctions* are displayed in Table I. One observes that the relaxation energy plays a dominant role in determining the Ge $3p_{3/2}$ level shifts. This is apparent in the series $Ge(CH_3)_4$, GeH_3CH_3 and GeH_4 where the GPM approach fails to reproduce the experimental trend. The explicit inclusion of the relaxation puts the calculated values on line with the measured data. An analysis in terms of the germanium effective charges and Madelung contribution to the $3p_{3/2}$ level shifts is illuminating. They are compared with the corresponding entities appearing in equivalent core and transition potential methods in Table II. It is apparent that the Ge ground state effective charges increase along the series GeH_4, GeH_3CH_3 and $Ge(CH_3)_4$ because the methyl group is in this case a better electron acceptor than hydrogen. By using the simple concept that a larger effective

TABLE II

Comparison Between the Ground State Effective Charges of Ge and Madelung Term and the Corresponding Entities Appearing in Equivalent Core and Transition Potential Methods[a]

Molecule	q(SCC)	q(e.c.)	q(t.p.)	M	M(e.c.)	M(t.p.)
GeH_4	0.16	0.35	0.35	—0.10	0.10	0.10
GeH_3CH_3	0.24	0.37	0.34	—0.14	0.08	0.08
$Ge(CH_3)_4$	0.46	0.43	0.36	—0.23	0.01	0.05
GeF_4	1.20	1.27	1.27	—0.72	—0.47	—0.46
GeH_3Cl	0.28	0.43	0.43	—0.14	0.06	0.06
$GeCl_4$	0.56	0.63	0.62	—0.26	—0.06	—0.06
GeH_3Br	0.22	0.38	0.38	—0.12	0.08	0.08

[a] Effective atomic charge is defined as $q_A = Z_A - n - Q_A$ where n is a number inner-core electrons and Q_A is gross valence electrons atomic charge. The average effective atomic charge in equivalent core method is given by q_A (e.c.) = (q_A (e.c.) + q (SCC))/2. Effective charges and Madelung terms are measured in | e | and eV, respectively.

* Simple sp basis set was employed.

positive charge means lesser electron repulsion on the host atom one can deduce that the $3p_{3/2}$ level in $Ge(CH_3)_4$ is lower than in GeH_4 and GeH_3CH_3. Contradiction with the experiment indicates that relaxation energy changes are responsible for the ESCA shifts. This is obvious from the results of the equivalent core and transition potential calculations (Table II). The charges q(e.c.) and q(t.p.) again change in the wrong direction but the differences are considerably less pronounced. On the other hand, the relaxation due to the flow of charge involved in the Madelung term overcompensates the one-center contributions of the Ge atoms and stabilizes GeH_3CH_3 and GeH_4 levels relative to that in $Ge(CH_3)_4$ establishing a semiquantitative agreement with experimental measurements. The rest of the data for GeF_4, GeH_3Cl, $GeCl_4$ and GeH_3Br are compatible with the simple rule of thumb that a larger effective positive charge q_{Ge} causes lower $3p_{3/2}$ levels, the most stable one being that in GeF_4. It is of some interest to compare our results with earlier findings of Perry and Jolly[12]. Their EHT calculations exhibit the same standard deviation of 1.2 eV for the the GPM approach but the relaxation process is much better described by the SCC-MO method (Table I). The CNDO/2 results are not improved by the inclusion of the relaxation energy but the GPM results were already quite good ($\sigma \sim 0.5$ eV) what is comparable with the standard deviation of our SCC-MO RP approach ($\sigma \sim 0.4$ eV). Good performance of the CNDO/2 method is probably a consequence of the special parametrization adopted by Perry and Jolly in their attempt to encompass the atoms of the second and third rows[12]. Namely, CNDO/2 results are generally inferior to the SCC-MO ones for the first row atoms[8]. The possible reasons are briefly discussed at the end of this section. It is worth to mention that the equivalent core and transition potential methods yield similar results (Tables I and II) as could be anticipated on the basis of a general analysis of Goscinski and Siegbahn[13]. The trend observed in this family of compounds parallels that found in a series of alkanes[14]. Pireaux et al.[14] established experimentally that binding energies decrease with an increase in number of carbon atoms in linear *n*-alkanes C_nH_{2n+2}. The whole range of the shifts is, however, small (0.6 eV). Ab initio calculations employing STO-4.31 G basis set have shown that the net charges of the central carbon atoms slightly increase along the series[14]. Since the binding energies decrease it means that the simple rule of thumb does not work here exactly as in the case of methylated germanes. The changes in BE are apparently governed here by the relaxation energies. Indeed, CNDO/2 calculations using transition potential formalism as well as Δ SCF ab initio equivalent core treatment have shown that changes in Madelung potentials, caused by the creation of a positive hole, are responsible for the observed trend[14]. It should pointed out, however, that in both calculations the relaxation energies had to be scaled by using a factor of 0.5 in order to restore the agreement between the theory and experiment. This is not surprising because the ab initio Δ SCF calculations were executed employing poor minimum STO-3G basis set while it is known that the basis sets close to the double zeta quality are a necessary prerequisite for obtaining reasonable estimates of relaxation energy[15]. Our search through the literature revealed also that CNDO/2 gives good ESCA shifts for a particular series of molecules if the adjustable parameters in the electrostatic formula are specially fitted for this purpose. However, these parameters widely differ from one series to another. Hence the general performance of the CNDO/2

method is not satisfactory. This can be ascribed to some inherent inconsistencies of this semiempirical scheme which in fact has not the proper theoretical structure while for example SCC-MO method does have it[16]. To conclude, the rule of thumb, according to which the higher net charge of the host atom corresponds to the increased inner-shell binding energy, is a good qualitative criterion if relatively large differences in charge along the series of compounds are expected. It fails, however, if the net charges of the atom suffering the ionization differ only slightly while in the same time more and more atoms participate in the relaxation process.

Finally, it should be stressed that the procedure adopted in this paper is only a model which mimics the more rigorous SCF treatment. It is based on the fictitious concept of point charge and its success lies in a fact that the $1/r$ operator is insensitive to the finer details of the electronic charge distribution[17,18]. Similar insensitivity of the one one-electron operator, which are otherwise extremely delicate probes of the electron charge density in various regions of molecules, was observed for second moments and the related diamagnetic part of the magnetic susceptibility[19,20]. The latter can be also satisfactorily accounted for by the point charge approximation.

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SAŽETAK

Semiempirijski studij energijskih razina elektrona unutrašnjih ljuski. Dio 7. ESCA pomaci $3p_{3/2}$ razina germanija u molekularnim sustavima

Z. B. Maksić i K. Rupnik

Pomaci energijskih $3p_{3/2}$ razina germanija u molekularnim sustavima razmatrani su primjenom semiempirijske metode samousaglašenog naboja (SCC-MO). Računi su izvršeni u okviru modela elektrostatskog potencijala u približenju točkastog naboja. Relaksacijske energije uzete su eksplicite u obzir korištenjem metoda ekvivalentnih jezgri i prelaznog potencijala. Ustanovljeno je da relaksacijske energije imaju odlučujuću ulogu u određivanju ESCA pomaka u nizu $GeH_4 \rightarrow Ge(CH_3)_4$. Rezultati dobiveni metodama ekvivalentnih jezgri i prelaznog potencijala su u dobrom slaganju s eksperimentalnim podacima.

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