

BOND ENERGY CALCULATION FOR THE NEGATIVE IONS OF HEAVY ELEMENTS

A. V. Glushkov, V. A. Efimov, A. N. Polevoy,
L. A. Vitavetskaya, Yu. V. Butenko,
A. V. Malinovskii, and E. A. Ryazanov

UDC 539.185

Electron bond energies are calculated for the negative ions of complex heavy elements Ge, Sn, Pb using the polarization potential formalism and relativistic perturbation theory of Rayleigh–Schrödinger type with a model potential of zero-order approximation. Basic correlation effects: polarizing interactions of outermost particles via the polarized core and mutual screening of outermost particles are taken into account to provide an acceptable accuracy of calculations. The paper gives refined values for the negative ions involved.

1. As is known, electron bond energy in negative ions (NI) is one of the most important characteristics which are essential for solving physicochemical problems and various applications (e.g., [1, 2]). The existing experimental methods do not provide the required accuracy to cover a wide range of ions as needed for applications, although the accuracy of measurements has considerably improved during recent years. Modern *a priori* quantum chemical methods are acceptable for calculating the spectra, transition energies, ionization potentials, and splitting of states, but bond energy calculations for NI is a rather complex problem. Using simplified models [1, 2] for solving this problem does not always give sufficiently accurate results to satisfy the requirements of applications.

Most NI may not be correctly described at all if one uses a one-particle (e.g., Hartree–Fock) approximation, since the total HF energy of the ions is higher than the HF energy of the ground state of an atom. Thus correct calculations of NI require that many-body correlation effects be taken into account.

It seems that methods of many-body theory are most consistent. In particular, there is an approach using a solution of Dyson's equation with a correctly defined self-energy function Σ ; however, this requires accurate and rather cumbersome calculations of the contributions of different effects to Σ . Among other approaches are the many-configuration HF approximation and the density functional approximation [2-9]. In a series of papers [10-18], new effective methods for calculating the structures and properties of atomic systems, including bond energy calculations for NI, were developed. They are based on the polarization potential formalism and relativistic perturbation theory (PT) with a model potential of zero-order approximation.

Earlier, these methods were widely used for precision calculations of the energy characteristics of atoms, ions, and molecules. They were modified and adapted [16-18] for calculations of NI and positive molecular ions including correlation effects. The methods were tested to calculate the electron bond energy in Na^- and NI of inert gases, rare earth elements, and the positive ions of alkaline metal dimers; it was demonstrated that the method is highly accurate and procedures for inclusion of correlation effects are correct. An important feature of the method is simultaneous allowance for exchange correlation and relativistic effects. The latter are especially important in the case of heavy NI.

Here we report on the results of bond energy calculations carried out by this method for the NI of heavy elements: Si, Ge, Sn, Pb, which are rather complex from the viewpoint of calculating electron correlation effects. The bond energies of these NI are given in [1] with an error of $\approx 30\%$. Thus it seems important that the bond energies be calculated more accurately to refine the values for the NI in question.

2. Since the computation procedure was described in previous papers (for details, see [16-18]), we consider

only several general points of prime importance. To determine the stability of NI and find the electron affinity for an atom, it is required to calculate the ground state energy of the ion A^- and to know the energies of the neutral atoms, respectively. A correct calculation of electron bond energy in NI demands that electron correlation effects playing a major role in the given problem be adequately included in the calculation. These effects are taken into consideration as higher-order perturbation theory effects starting from the second-order effect using the formalism of polarization potential and relativistic perturbation theory with a model potential of zero-order approximation.

The computation code permits one to calculate the energy matrix within the scheme of $j-j$ coupling of angular momenta; a transition to the intermediate scheme of coupling is effected by diagonalizing a secular matrix. The states of NI and the corresponding neutral (in the ground state) atom with which we are concerned may be regarded as three- and two-particle states (with three p -electrons and with two p -electrons over the core of completed shells, the configuration of the system having no np^3 and np^2 outermost shells in the ground state).

The energy of the two-particle state is represented as a PT series:

$$E(n_1 l_1 j_1, n_2 l_2 j_2) = E_{el}^{(0)}(n_1 l_1 j_1) + E_{el}^{(0)}(n_2 l_2 j_2) + \Delta E^{(1)} + \Delta E^{(2)} + \dots \quad (1)$$

In the case of the three-particle state (with 3 electrons), the corresponding energy is defined as

$$E(n_1 l_1 j_1, n_2 l_2 j_2 [J_{12}], n_3 l_3 j_3) = E_{el}^{(0)}(n_1 l_1 j_1) + E_{el}^{(0)}(n_2 l_2 j_2) + E_{el}^{(0)}(n_3 l_3 j_3) + \Delta E^{(1)} + \Delta E^{(2)} + \dots, \quad (2)$$

where J_{12} is the intermediate momentum of coupling of two electrons; $E_{el}^{(0)}(nlj)$ are the one-particle energies of one electron over the core of closed shells (calculated with respect to the core energy). The desired one-particle energies are determined by the ionization potentials of the ions of neutral atoms (Si^- , Ge^- , Sn^- , Pb^-) corresponding to the given NI and the energies of electron transition over the core in these atoms. The one-particle energies $E_{el}^{(0)}(nlj)$ contribute to only diagonal elements. These one-particle energies are easily and sufficiently accurately reproduced by the methods used in this paper.

Here it is appropriate to use experimental data in the zero-order approximation of PT. This leads to implicit inclusion of many correlation and relativistic effects and permits one to generate an optimal basis in the zero-order approximation of PT; the basis is used further in calculations of the matrix elements of first- and second-order PT. The one-particle functions of the zero-order approximation were determined by numerically solving Dirac's relativistic equation with a model potential $V_c(r)$ describing the interaction of the outermost electron (quasiparticle) with the atomic core of completed shells. As V_c we took a potential [19]

$$V_c(r) = -\{Z - 2[1 - \exp(-2r)(1+r) - (N-2)] \times [1 - \exp(-br)(1 + 0.75br + 0.25b^2r^2 + 0.0625b^3r^3)]\} / r \quad (2.5), \quad (3)$$

where N is the number of electrons in the core; the constant b is determined either from the known values of the energy levels of the ion or using an *ab initio* procedure [20], which is actually the same. The PT perturbation operator is of the form

$$V_{int}(r_i r_j) = \sum_{i,j} \exp(i|\omega|r_{ij})(1 - \alpha_i \alpha_j) / r_{ij} - \sum_i V_c(r_i), \quad (4)$$

where α_i, α_j are the Dirac matrices. Recall that the exponential multiplier $\exp(i|\omega|r)$ here defines the effects of lagging in interaction.

In first-order PT, it is necessary to calculate the matrix [for correction $\Delta E^{(1)}$, see (1)] of the electron–electron interaction operator and of the electron–electron–electron interaction operator [for correction $\Delta E^{(2)}$, see (2)]. The operator is represented as a sum of the matrix elements of electron–electron interaction. The first-order matrix element of the electron–electron interaction operator is

$$M_1 = \langle n_1 l_1 j_1 n_2 l_2 j_2 [J] | V_{int} | n_4 l_4 j_4 n_3 l_3 j_3 [J] \rangle = P_1 P_2 (-1)^{1+j_2 j_4 + J} [(2j_1 + 1)(2j_2 + 1)(2j_3 + 1)(2j_4 + 1)]^{1/2} \sum_{i,k} \sum_a \begin{Bmatrix} j_1 & j_k & J \\ j_2 & j_1 & a \end{Bmatrix} (\delta_{i,3} \delta_{k,4} + (-1)^J \delta_{i,4} \delta_{k,3}) Q_a(12;43), \quad (5)$$

$$P_1 = \begin{cases} 1 & \text{for } n_1 l_1 j_1 \neq n_2 l_2 j_2, \\ 1/2 & \text{for } n_1 l_1 j_1 = n_2 l_2 j_2, \end{cases} \quad P_2 = \begin{cases} 1 & \text{for } n_3 l_3 j_3 \neq n_4 l_4 j_4, \\ 1/2 & \text{for } n_3 l_3 j_3 = n_4 l_4 j_4, \end{cases}$$