A search for the quantum-chemical methods of germanium-oxygen geometric structure calculation

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Abstract. The methods of density functional theory (DFT in Kohn-Shem formalism) currently play the role of main instruments of quantum chemistry. The examination of the oxygen atoms behavior in germanium requires preliminary calibration of the functionals for less resource-intensive problems. With this end calibration of the germanium exchange and correlational functionals was made for the finite calculation of such parameters as oscillation frequencies, dipole moment, full electron energy. A correlation was found between the calculated values of Ge-O bond lengths and harmonic oscillation frequency. The functionals for further study of the oxygen behaviour in crystalline germanium were determined.

1. Introduction
The first step of quantum-mechanical calculations of physico-chemical properties of a compound always starts from the optimization of its equilibrium structure. By now a rather large number of models and methods exist in the disposal of quantum chemistry. This variety is explained by the fact that one or another approximation is introduced during the derivation of equations thus narrowing the sphere of applicability of the specified model. As a result the studies of new properties or classes of substances were accompanied by the development of modified methods.

Crystalline germanium is an inherent part of a large number of semiconductor instruments, units and elements of infrared optics and photonics. As this takes place the creation of modern element base will be impossible without the use of single crystals having low and ultralow concentration of impurities. For example, crystals for detectors of ionizing irradiation require electroactive impurity concentration below $10^{10}$ cm$^{-3}$. In addition germanium always contain background impurities, such as oxygen with a concentration of up to $10^{17}$ cm$^{-3}$, carbon, nitrogen, etc. Oxygen impurity results in a formation of dislocations, microdefects and thermal donors, which in its turn have an influence on the lifetime of nonequilibrium charge carriers [1, 2].

Calculations of the structure and properties of bulk crystalline bodies are based on the selection of the optimal method/basis combination [3] reproducing the geometry of the object under study with the required accuracy: the bond length inaccuracies should not exceed 0.01 Å, and those of valent and dihedral angles should be less than 5 and 10 degrees, respectively. Large errors in the equilibrium geometry result, as a rule, in divergence of such parameters as oscillation frequency, dipole moment and full electron energy, which have an effect on the overall values of the entropy, enthalpy, free Gibbs energy, etc.
2. Method of calculation

The methods based on the Hartree-Fock model (MPn, QCI, CC), and those of the density functional (DFT in Kohn-Shem formalism) (DFT в формализме Кона-Шема) at the moment play the role of main quantum chemistry instruments. The former put into the foreground more productive computer analysis given above we calculated the harmonic frequency combination of existence of several isotopes of both elements comprising natural samples of GeO. Nevertheless into wide bands with the increase of the temperature. The complexity of the spectrum is related to the parameters of germanium.

Germanium oxide GeO is the most simple composition for making an estimation of the geometric resource-intensive tasks is required for the investigation of oxygen atom behavior in germanium. The spectrum of gaseous germanium oxide is characterized by a large number of lines merging into wide bands with the increase of the temperature. The complexity of the spectrum is related to the

| Method/basis | \( r(GeO) \), Å | \( \Delta, \) Å | Method/basis | \( r(GeO) \), Å | \( \Delta, \) Å |
|--------------|-----------------|-----------------|--------------|-----------------|-----------------|
| B3LYP/SVP    | 1.632 [5]       | 0.007           | B97/6-311+G(2df) | 1.601 [10]       | -0.024          |
| B3LYP/6-31G(d) | 1.647 [6]       | 0.022           | MB97/6-311+G(2df) | 1.601 [10]       | -0.024          |
| B3LYP/cc-pVQZ | 1.634 [7]       | 0.009           | HCTH/6-311+G(2df) | 1.637 [10]       | 0.012           |
| B3LYP/SVP    | 1.632 [8]       | 0.007           | TPSS/cc-pVQZ    | 1.643 [7]        | 0.018           |
| B3LYP/SVP+f  | 1.624 [8]       | -0.001          | LSDA/ECP       | 1.563 [11]       | -0.062          |
| B3LYP/DZP    | 1.636 [8]       | 0.011           | LDA/ECP        | 1.593 [12]       | -0.032          |
| B3LYP/DZP+f  | 1.628 [8]       | 0.003           | LDA/6–31+G(3df,3pd) | 1.627 [12]     | 0.002           |
| B3LYP/6-311G** | 1.630 [8]     | 0.005           | BLYP/SVP       | 1.655 [8]        | 0.030           |
| B3LYP/6-311G | 1.648 [9]       | 0.023           | BLYP/SVP+f     | 1.648 [8]        | 0.023           |
| B3LYP/6-311+G(2df, 2pd) | 1.633 [9] | 0.008           | BLYP/DZP       | 1.660 [8]        | 0.035           |
| BPW91/6-31G(d) | 1.664 [6]       | 0.039           | BLYP/DZP+f     | 1.652 [8]        | 0.027           |
| B3PW91/6-31G(d) | 1.642 [6]       | 0.017           | BLYP/6-311G**  | 1.653 [8]        | 0.028           |
| LHF/6-311+G(2df) | 1.591 [10]    | -0.034          | BLYP/cc-pVQZ   | 1.657 [7]        | 0.032           |
| B972/6-311+G(2df) | 1.622 [10]   | -0.003          | BLYP/6-31G(d)  | 1.671 [6]        | 0.046           |
| MB97-2/6-311+G(2df) | 1.622 [10]  | -0.003          | Phenomenological calculations | 1.714 [13] | 0.089|

The consideration of Table 1 shows that the required accuracy may be achieved by the use of functionals MB97-2, B972, B3LYP and LDA. The DFT provides a possibility of obtaining the required geometrical parameters, which give an opportunity to calculate other physico-chemical parameters of germanium. The spectrum of gaseous germanium oxide is characterized by a large number of lines merging into wide bands with the increase of the temperature. The complexity of the spectrum is related to the existence of several isotopes of both elements comprising natural samples of GeO. Nevertheless combination of \( ^{72}\text{Ge}^{16}\text{O} \) is used in most calculations of the properties. Starting from the performed analysis given above we calculated the harmonic frequency \( (\omega_{\text{harm}} \text{, Table 3}) \) for the chosen set of isotopes and compared it with the \( \omega_{\text{harm}} \) estimated by the experimental spectrum [15]. The divergence in the calculated length resulted in a divergence in \( \omega_{\text{harm}} \) (Table 3). The values most close to the experimental \( \omega_{\text{harm}} \) ones were given by functionals XAlpha, VSXC and SVWN.
Table 2. \( r(\text{Ge-O}) \) bond lengths in gaseous germanium oxide found in the basis of 6-311+G(3df, 3pd) 6d 10f. \( \Delta \) is the error of the calculation.

| Method   | \( R(\text{GeO}), \AA \) | \( \Delta, \AA \) | Method   | \( R(\text{GeO}), \AA \) | \( \Delta, \AA \) |
|----------|-----------------|----------------|----------|-----------------|----------------|
| SVWN     | 1.624           | 0.000          | B972     | 1.623           | -0.001         |
| VSXC     | 1.638           | 0.013          | B3LYP    | 1.631           | 0.007          |
| XAlpha   | 1.628           | 0.003          | B3PW91   | 1.626           | 0.001          |
| HFS      | 1.645           | 0.020          | MPW1PW91 | 1.621           | -0.003         |
| HCTH     | 1.636           | 0.012          | PBE1PBE  | 1.622           | -0.003         |
| B3P86    | 1.624           | -0.001         | BHandH   | 1.596           | -0.029         |
| HFB      | 1.677           | 0.052          | BHandHLYP| 1.608           | -0.016         |
| B1B95    | 1.620           | -0.005         | M06      | 1.623           | -0.001         |
| B1LYP    | 1.629           | 0.004          | B2PLYP   | 1.648           | 0.023          |
| BLYP     | 1.655           | 0.030          | mPW2PLYP | 1.641           | 0.017          |
| B98      | 1.627           | 0.003          | MP2(FC)  | 1.662           | 0.037          |
| B971     | 1.630           | 0.005          | MP2(FULL)| 1.644           | 0.020          |
| experiment | 1.625             |                | BPW91    | 1.646           | 0.021          |

Table 3. Theoretical harmonic frequencies (wave numbers) of \(^{16}\text{Ge}^{16}\text{O} (\omega_{\text{harm}}), \text{cm}^{-1}\).

| Method   | \( \omega_{\text{harm}} \) | Method   | \( \omega_{\text{harm}} \) | Method   | \( \omega_{\text{harm}} \) | Method   | \( \omega_{\text{harm}} \) |
|----------|-----------------|----------|-----------------|----------|-----------------|----------|----------------|
| HFB      | 893             | VSXC     | 978             | B972     | 1015            | BHandHLYP| 1071           |
| BLYP     | 937             | XAlpha   | 983             | B98      | 1017            | BHandH   | 1098           |
| HFS      | 954             | SVWN     | 996             | B3P86    | 1017            | UMP2-FC  | 947            |
| B2PLYP   | 954             | B3LYP    | 999             | M06      | 1018            | MP2(FULL)| 954            |
| BPW91    | 956             | B1LYP    | 1009            | PBE1PBE  | 1025            |          |                |
| HCTH     | 962             | B971     | 1012            | MPW1PW91 | 1026            |          |                |
| mPW2PLYP | 974             | B3PW91   | 1013            | B1B95    | 1028            | \( \omega_{\text{harm}} [15] \) | 985.5    |

The calculated harmonic frequencies rarely coincide with the experiment, especially for motions having large amplitudes. As a rule, the deviations from the experiment larger than 15 cm\(^{-1}\) results in calculation errors in thermodynamical properties reaching a maximum in the high-temperature region. In this view a large part of \( \omega_{\text{harm}} \) (Table 3) needs to be corrected by scaling. In terms of performed calculations it becomes possible to introduce scaling coefficients for each functional and further apply them for the determination of germanium oxide properties. Our next step in the study of oxygen and germanium interaction will be the determination of GeO thermodynamical functions in the temperature interval of 298-1500 K.

3. Conclusion

Analysis of the Tables 1 - 3 enables to recommend the use of the following functionals MB97-2, B972, B3LYP and LDA(SVWN), XAlpha, B3P86, B1B95, B1LYP, B98, B971, B3PW91,
MPW1PW91, PBE1PBE, M06 for the study of oxygen behavior in crystalline germanium.

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