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A quantum theory of the thermodynamic functions of a molecular gas in a vibrational potential approximation in the form of the Gaussian exponential

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Abstract

A general method of solving the wave Bloch equation for the molecular gas statistical density matrix in an arbitrary temperature interval has been suggested. As a base of the method the Green function for a harmonic oscillator and a model of vibrational molecular potential in the form of the exponential on quadratic force field have been used.

The statistical density matrix or the statistical sum for molecular ensemble is a fundamental function of quantum theory of substance thermodynamic properties which takes into consideration not only translational degrees of freedom of molecules in gas, but inner molecular quantum states, also. Determining spectral part for the substance thermodynamic properties prove to be the low lying regions of the electromagnetic spectrum to whom the vibrational states of atoms in molecules correspond, that is connected with the exponential dependence of the statistical sum on eigenvalues of the Schroedinger equation.

In our method the statistical Bloch equation has been employed in its integral form and solving of which is realized by iterations. The latter proved to be fruitful one for solving the problem of calculation the thermal averages of vibrational coordinate powers by which one can model the molecular vibrational potential. An initial iteration approximation was chosen in the form of harmonic oscillators. The calculation of the integral operator kernels is substantially facilitated by the Gaussian form of the Green function of the Bloch integral equation. It is this circumstance that proved to be decisive when choosing a generated model for anharmonic vibrational potential in the form of the exponential on harmonic potential that reduced to calculation in closed form of all the matrix elements of the iteration scheme at any values of the absolute temperature.

An important property of the suggested method for the calculation of the statistical sum for a molecular gas is the regular behavior of all the calculated averages in dependence on combinations of eigen vibrational frequencies. The previous semiempirical and semiclassical methods of calculating the thermal averages reduced to expressions which diverged at the Fermi resonances.

In our work we have obtained the formulae for the statistical sum and the thermodynamic functions of molecular gases up to the second iteration included that makes it possible a theoretical analysis and prediction of the thermophysical and thermochemical properties of polyatomic molecular gases at any temperatures.

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