Computation of molecular spectra and thermodynamic functions for diatomic ideal gases using interatomic potentials

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Abstract. A method for calculation of the thermodynamic properties of diatomic ideal gases using interatomic interaction potentials is discussed. For instance the computation of thermodynamic functions such as heat capacity, entropy and reduced Gibbs energy in the temperature range 298.15–10 000 K is shown for diatomic argon compounds.

1. Introduction
Data on thermodynamic properties of pure substances play an important role in nuclear power engineering, chemical industry, metallurgy, etc. To systematize a vast amount of such data, there is a need for active development of modern databases. Examples of the thermodynamic databases of pure substances are the Chemical WebBook of the National Institute of Standards and Technology, USA [1], the databases of Scientific Group Thermo Europe and the IVTANTHERMO project developed in the Joint Institute for High Temperatures of the Russian Academy of Sciences [2–4] based on the reference book [5].

According to the principles formulated in [2], thermodynamic databases based on the critical analysis of the experimental data must be regularly updated. Therefore there is a need for developing methods of calculating the thermodynamic properties and for creating new codes to implement these methods. In particular, the latest advances in quantum chemistry provide new information about the structure and energy levels of molecules which can be used to calculate the thermodynamic properties when experimental data are missing or unreliable.

The calculation of the thermodynamic properties of diatomic gases is based usually on the values of molecular constants. This technique is described, for example, in the reference book [5] and is used in many other works. However, two problems arise: absence of reliable experimental data for some substances and using a simple model of the interatomic interaction potential which is typically the Morse potential [6]. At the same time there are substances, such as weakly bound molecules with low dissociation energy, for which this model can be incorrect and lead to significant uncertainties for resulting thermodynamic functions.

In this work, we discuss another method based on the use of interatomic potentials for calculating thermodynamic functions of diatomic ideal gases. The method was applied to study...
diatomic compounds of argon (argides) as most of them are weakly bound molecules. The thermodynamic functions and updated formation enthalpies were calculated for the following substances: ArCo$^+$ and ArV$^+$ [7], Ar$_2^+$ and Ar$_2$ [8], ArH$^+$ and ArH [9], ArO and ArO$^+$ [10]. Theses compounds play an important role in the mass spectrometry with inductively coupled plasma [11].

The method includes few steps:

(i) literature study of experimental and ab initio data of interaction potential for the ground and excited electronic states;

(ii) approximation of the initial data of the interaction potential by a smooth analytical curve;

(iii) numerical solution of the stationary Schrödinger equation to obtain rovibronic energy levels;

(iv) filtering out the eigenfunctions that do not correspond to real electronic states;

(v) calculation of the partition function and main thermodynamic functions depending on the temperature;

(vi) fitting the thermodynamic functions to polynomials or other functions used to represent the thermodynamic data in databases.

This procedure is performed iteratively for each electronic states and followed by an analysis of the results to find those electronic states which have reliable initial data and influence the final thermodynamic functions. The sections below describe steps ii to vi in more details. The algorithm is illustrated by the calculation results for particular molecules such as ArO$^+$ and ArO, although the full studies of these molecules are given in the corresponding papers (see [10] for ArO$^+$ and ArO).

2. Approximation of the potential curve

Source data upon the interatomic potential for a diatomic molecule can be obtained both from direct ab initio calculations and from semi-empirical models that use the results of experimental spectral studies. As far as calculation of the thermodynamic functions requires the interaction potential to be a smooth analytical curve, in both cases the source data must be approximated to a certain model of interatomic interaction.

The simplest way to obtain a smooth curve (implemented also in the LEVEL code) is to use spline fitting. Typical problems here are the insufficient number of points at low interatomic distances and the lack of data for extrapolation to the dissociation limit at large distances. In this case, the spline interpolation leads to oscillations that can add inaccuracies in the resulting rovibrational spectrum. Therefore approximation of the data by a predetermined model of interatomic interaction is preferred.

A large number of mathematical models of potential curves are presented in the literature [12–14]. Let us consider the Hulburt–Hirschfelder potential [14], which is a modification of the Morse potential and has the following form:

$$V(r) = D_e [1 - e^{-x}]^2 + D_e c x^3 (1 + bx e^{-2x}),$$

$$x = \frac{\omega_e}{2(B_e D_e)^{1/2}} \frac{r - r_e}{r_e},$$

$$c = 1 - \frac{f}{\alpha_1}, \quad b = 2 - \frac{1}{12c} \left[ 7 - \frac{1}{\alpha_1^2} \left( 15 f^2 - 8 \frac{\omega_e x_e}{B_e} \right) \right], \quad f = 1 + \frac{\alpha_1 \omega_e}{6B_e^2},$$

where $D_e$ is the dissociation energy of the molecule, $\omega_e$ is the vibrational constant, $B_e$ is the rotational constant, $r_e$ is the equilibrium internuclear distance, $\alpha_1$ is the first constant of the vibrational-rotational interaction, $\omega_e x_e$ is the constant of anharmonicity. The first term in equation (1) corresponds to the original Morse potential.

In comparison with the widely used Morse potential, the Hulburt–Hirschfelder potential has a number of advantages for describing anharmonic vibrations of molecules. In particular, it reproduces the local maximum of the potential energy function.
Figure 1. Approximation of the potential curve for ground electronic state of the ArO$^+$. Empty circles are the digitized values of the potential energy depending on the distance [16], grey line represents the EMO potential, obtained from the digitized data.

By approximating the source data using this mathematical model one can obtain the values of molecular constants. An example is given in [15] where the authors calculated the energies of the low-lying electronic states of the Ar$^+_2$. Then, for each state, the authors scanned the potential energy values and approximated the results to potential (1).

Another example of such approximation is shown in figure 1 (where the potential $V$ values are expressed in cm$^{-1} = 1.2399 \times 10^{-4}$ eV). In this case the ground state of the ArO$^+$ was approximated, using EMO (extended Morse oscillator) potential [13]:

$$V(r) = D_e \{1 - \exp[\beta(r)(r - r_e)]\}^2, \quad \beta(r) = \sum_{i=0}^{N_{\beta}} \beta_i \left[y_{\text{ref}}^i(r)\right]^i, \quad y_{\text{ref}}^i(r) = \frac{r_q - r_{\text{ref}}}{r_q + r_{\text{ref}}},$$

(2)

where $D_e$, $r_e$ have the same meaning as in (1), and $\beta_i$, $q$, $N_{\beta}$, $r_{\text{ref}}$ are varied parameters. It allows determining data in the areas where there is a lack of source points, in particular at large distances.

3. Numerical solution of the Schrödinger equation

The next step in calculation of the thermodynamic functions is the numerical solution of the radial Schrödinger equation:

$$-\frac{\hbar^2}{2\mu} \frac{d^2 \Psi_{v,j}(r)}{dr^2} + V_J(r) \Psi_{v,j}(r) = E_{v,j}(r),$$

(3)

$$V_J(r) = V_0(r) + \left(\frac{\hbar}{8\pi^2 \mu c}\right) J(J + 1) \frac{1}{r^2},$$

(4)
where $\mu$ is the reduced mass of the molecule, $J$ is the rotational quantum number, $v$ is the vibrational quantum number, $V_0(r)$ is the rotationless potential of the interatomic interaction. There is a variety of rotationless potential models in addition to those presented in section 2. The described algorithm allows to use all the potentials implemented in the LEVEL code [17], including the spline approximation of an arbitrary set of points.

The LEVEL [17] code can be used to determine the rovibrational spectrum of the molecule. This program allows calculating the rovibrational energy levels and represents their values as

$$E_{v,J} = G(v) + B_v[J(J + 1) - \Omega^2] - D_v[J(J + 1) - \Omega^2]^2 + H_v[J(J + 1) - \Omega^2]^3 + \cdots$$

where $\Omega$ is the projection of the electron angular momentum on the interatomic axis.

The results of calculations of the rovibrational spectrum have the form (5), which is a seventh-degree polynomial with respect to the quantum number $J$. This approximation function is provided by the LEVEL code without any restrictions to the values of $v$ and $J$. For instance, it may decrease with an increase in the quantum number $J$ which is a computational artefact and does not correspond to the real solution of equation (3). Determination of a proper set of the combinations of $\{v, J\}$ is the next task performed by our own code.

First when calculating the partition function, it is necessary to use only those energy levels that meet the requirement of monotonous growth of the energy both for the vibrational number $v$ and for the rotational number $J$.

Another requirement for filtering of energy levels comes from the effective potential form (4). Figure 2 shows the example of the effective potential for CH$^+$ with rotation [18]. For some values of $J$, the potential curve may have a local maximum. However, the energies represented in the form (5) may lie above the energy of the local maximum thus it is necessary to sum up the energies of only those levels that lie below the energy of the local maximum.

4. Calculation of thermodynamic functions

After selection of the correct rovibrational levels for all considered electronic states, it is possible to calculate the internal partition function and the reduced Gibbs energy

$$Q_{\text{int}} = \sum_i g_i Q_{\text{vib-rot}}^i \exp[-(E_{0,0}^i - E_{0,0}^i)/k_B T],$$

$$Q_{\text{vib-rot}}^i = \sum_{v,J} (2J + 1) \exp[-(E_{v,J}^i - E_{0,0}^i)/k_B T],$$

$$\Phi_{\text{int}}^0(T) = -\frac{G(T) - H(0)}{RT} = \ln(Q_{\text{int}}),$$

where $i$ is the electronic state number, $g_i$ is the statistical weight of this state, $G(T)$ is the Gibbs energy and $H(0)$ is the enthalpy value at $T = 0$ K. Some reference books use also the values of thermodynamic functions at the standard temperature $T = 298.15$ K. Here we follow the definitions of the book [2] and use $T = 0$ K as the origin.

The dependence of the Gibbs energy on temperature is obtained from the partition function and the reduced Gibbs energy are then it is approximated by functions traditionally used in the IVTANTHERMO database [5]:

$$\Phi^0(T) = \phi_1 + \phi_2 \ln X + \phi_3 X^{-2} + \phi_4 X^{-1} + \phi_5 X + \phi_6 X^2 + \phi_7 X^3,$$

where $X = 10^{-4} T$. This approximation usually requires to use few temperature intervals to represent the calculated data with a good accuracy. In order to determine the number of such intervals along with their boundaries a special algorithm is used which determines these values depending on a given accuracy [4].
Figure 2. Centrifugally distorted potential with \( J = 32 \) for the \((^1\Pi)\) state of CH\(^+\) [18].

The upper temperature boundary for the tables obtained from equation (9) ranges from 5000 to 20000 K. Although most of the molecules dissociate at the upper temperature bound the small fraction of them still exist. Taking the thermodynamic functions of these molecules into account in the whole temperature range improves the accuracy of thermodynamic modelling [3].

The approximation (9) is needed mainly for further use of the thermodynamic functions stored in a database for thermodynamic modelling [3]. In the new database called “IVTANTHERMO-Online” [4] it is proposed to store all the details of the computations such as initial and approximated potential curves, sets of rovibrational energy levels for all electronic states, tables with the calculated values of the partition function and other thermodynamic functions depending on temperature (6). It allows to revise the calculation results easily when new experimental or \textit{ab initio} data appear or to obtain another approximation of the thermodynamic functions to achieve better accuracy or to use a different form of approximation functions.

Periodic updating the data in the IVTANTHERMO-Online database is of a great importance which also follows from the requirements for the “critical reference books” formulated by L V Gurvich [2]. To partially automate calculation of the thermodynamic functions of ideal diatomic gases one can use the algorithm described above supported by a code for visualization of the results at each calculation step.

There is a particular problem of selection of a proper number of electronic states to be taken into account in the final result. The procedure described above corresponds to the calculation of thermodynamic functions for a single electronic state. In some cases the contribution of the ground state is crucial and all other electronic states (typically high energy states) can be neglected. The examples are ArH\(^+\) [9], Ar\(_2^+\) and Ar\(_2\) [8]. In other cases low energy electronic states should be included (see the analysis of ArCo\(^+\) and ArV\(^+\) [7], ArO and ArO\(^+\) [10], ArH [9]). Therefore it is useful to view the change of the thermodynamic functions with subsequent
addition of exited electronic states which can be done using a special visualization module (figure 3). As input data for high energy states usually have worse precision than those for low energy states, cutting off the high energy levels can even improve the accuracy of the results. The visualization module is developed as a standalone application. In future it is planned to implement this module as a web application integrated with the IVTANTHERMO-Online database.

5. Conclusion
An algorithm for calculation of the thermodynamic properties of diatomic ideal gases based on the use of interatomic interaction potentials is presented. The use of this algorithm along with a corresponding visualization tool facilitates regular updates and extension of thermodynamic databases such as the IVTANTHERMO database using the latest experimental results and \textit{ab initio} calculations. The improvement of the database to store the row calculation data is proposed. The method was applied to a number of diatomic compounds of argon and showed its high productivity.

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