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DEVELOPMENT OF A GENERAL APPROACH TO THE MODELING OF FREE AND CONFINED POLYATOMIC SYSTEMS

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The concepts of the project ATOMSK are outlined. The project aims at developing a general approach to the theoretical study of free and localized polyatomic systems including the development of appropriate computational tools. Basic physical principles and general scheme of the approach are stated. Calculation of the energy states of molecular hydrogen in single-crystal silicon was considered as an example.

Keywords: polyatomic system, model, quantum state, ATOMSK.

INTRODUCTION

Spectroscopy is a reliable and effective instrument for investigation of the composition and properties of different objects and media. Owing to the universality of spectral analysis methods, the uniqueness of extracted information, and the possibility of *in situ* measurements, spectroscopy is widely used for solving both fundamental and applied problems.

With the development of science and technology the applicability of spectroscopic methods is constantly expanding its scope. On one hand, this is due to the development of physical concepts and the modernization of experimental equipment, which is becoming more advanced and precise. On the other hand, new objects of research arise together with new applications, new problems, and challenges. The development of high-performance computing systems, which allow spectroscopic data to be calculated and processed, plays one of the key roles. Besides, most of the computing resources are used to model and simulate different polyatomic systems. It should be noted that the theoretical calculations are needed to predict and interpret the experimental results and in some cases they are the only source of information on the system under study.

Currently there are a number of computer programs available for the calculation of rovibrational states of triatomic (MORBID [1], RENNER [2], DR [3, 4], DVR3D [5], EVEREST [6]), tetraatomic (TetraVib [7]) and polyatomic (TROVE [8], GENIUSH [9], MULTIMODE [10], ANGMOL [11]) free molecules. These programs are unable to deal with a fully arbitrary molecule mainly due to the limitations of mathematical models implemented in them and to computer limitations. Besides, due to the increase in the variety of systems (including those of an interdisciplinary nature) studied by spectroscopic methods, there is a huge number of problems that go beyond the approach of the free molecule. For example, in many cases molecules can be exposed to an external action from the ambient environment, they can be part of more complex systems, or can be adsorbed on the surface of or embedded in a crystal. Therefore, there is a need for computational tools to simulate spectra of polyatomic molecules in external force fields.

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Owing to the huge variety of molecular systems, the development of a single universal code with a high level of optimization and complete set of necessary theoretical models is a task too cumbersome and difficult to achieve at the moment. However, taking into account the nature of the objects in question and the increase in the number of interdisciplinary studies, there is a necessity to develop a general approach to modelling spectra of molecules with or without external fields. Therefore, it has been decided to initiate the ATOMSK project (it is an acronym of "ATOmistic Modeling Subroutines Kit"). This project aims to develop the required theoretical models and a cataloged package of routines and modules which can be used to construct a new FORTRAN program adjusted and optimized to do calculations for a specific polyatomic system.

1. CONCEPT

In the approach under development the system is considered within the framework of the adiabatic approximation, i.e. the problem is separated into electronic and atomic (nuclear) parts. At first, mainly using *ab initio* methods [12], the stationary Schrödinger equation for one or several isolated electronic states is solved, the structure and energetics of the system are analyzed, the model is constructed, and the potential energy of the atomic subsystem is determined. Further, depending on the objectives, the classical and/or quantum-mechanical consideration of the object under study is possible. Of course, this separation is conditional and in some cases electronic and nuclear equations can/should be addressed jointly. In this work we are restricted to report only the quantum-mechanical consideration of polyatomic systems. When a condensed medium is under study, different methods for solving the systems of classical equations of motion are also used, including such methods as molecular dynamics and Monte Carlo [13].

The appropriate Schrödinger equations are solved numerically using the variational approach. This approach is universal for the majority of quantum-mechanical objects and proved to be effective when applied to the polyatomic systems. The computational algorithm is constructed under a general scheme including the following main steps:

1) Development/revision of the mathematical model.
2) Selection of the coordinate system (normal, natural, curvilinear, etc.).
3) Construction of the system Hamiltonian.
4) Selection/calculation of the basis set functions (orthogonal polynomials, plane waves, etc.).
5) Calculation of the matrix elements (numerical and/or analytical integration).
6) Diagonalization of the Hamiltonian matrix.
7) Wavefunction analysis and calculation of the physical quantities and properties of interest.

It is clear that this scheme could be iteratively repeated a required number of times with the inclusion/exclusion of certain elements. If possible, the symmetry of the system is taken into account.

The nature of the localization determines the boundary conditions. For instance, when dealing with an object inside a crystal or at an interface, it is sometimes necessary to take into account the periodicity properties of the structure. In such cases, the best choice of the basis set for the translational degrees of freedom is plane waves.

The verification/validation of the models developed and the debugging of the program constructed are carried out mainly by comparison with the available experimental data as well as by detailed analyses of the results obtained. The structural elements of the program are tested on available textbook examples, including exactly integrable and limiting cases. When a new system is studied, a natural extension of the functionality and range of applicability of the software package ATOMSK takes place, and this ultimately contributes to the development of a general approach to the modeling of polyatomic systems.

2. EXAMPLE

Let us consider the calculation of the energy states of interstitial molecular hydrogen in single-crystal silicon as an example. The five degrees of freedom of the molecule (translational and rotational) are taken into account. A detailed study of the structural and energy properties of this system is presented in [14]. The potential energy function

TABLE 1. Rotational Term Values of an H_2 Molecule in Single-Crystal Silicon (cm^{-1})

l	5D model	2D model [15]	$B_0\,l(l+1)$	Exp. [16]
1	103.45 (T_2)	105.21 (T_{1u})	105.37	99
2	307.64 (T_2) 310.37 (E)	300.79 (E_g) 326.65 (T_{2g})	316.10	297
3	588.59 (A_1) 610.32 (T_2) 612.15 (T_1)	623.74 (T_{1u}) 634.63 (T_{2u}) 653.87 (A_{2u})	632.20	–

of the system versus the position and orientation of the interstitial defect is determined within the framework of the approach used in [14], including the model construction and the coordinate system selection.

Our Hamiltonian of the H_2–Si system has the following form:

$$\hat{H} = \frac{\hat{\boldsymbol{P}}^2}{2M} + \frac{\hat{\boldsymbol{L}}^2}{2\mu\rho^2} + V(\boldsymbol{R}, \theta, \varphi)\,, \tag{1}$$

where $\hat{\boldsymbol{P}}$ is the center-of-mass momentum operator of the hydrogen molecule with the total mass M, $\hat{\boldsymbol{L}}$ is the molecule angular momentum operator, ρ is the average H_2 bond length inside the crystal, μ is the molecular reduced mass. The function $V = V(\boldsymbol{R}, \theta, \varphi)$ is the corresponding potential energy, where θ and φ are spherical coordinates defining the orientation of the molecule and $\boldsymbol{R} = (X, Y, Z)$ are the Cartesian coordinates of the molecule center of mass. The Cartesian coordinate system is chosen such that its axis directions coincide with the supercell ones (see Fig. 1 in [14]). The value $\theta = 0$ corresponds to the orientation of H_2 along the Z axis.

In this example only the low lying energy states of the system were calculated; therefore, the Schrödinger equation with Hamiltonian (1) was solved only at the Γ point. The ansatz composed by the products of the plane waves and the spherical harmonics is defined by the following expansion:

$$\psi_n(\boldsymbol{R}, \theta, \varphi) = \sum_{\boldsymbol{G}, l, m} a_{lm}^n(\boldsymbol{G}) \exp(i\boldsymbol{G} \cdot \boldsymbol{R}) Y_l^m(\theta, \varphi)\,, \tag{2}$$

where $\boldsymbol{G}$ are reciprocal lattice vectors and $a_{lm}^n(\boldsymbol{G})$ are coefficients to be determined.

In the algorithm employed the matrix elements of Hamiltonian (1) are calculated in two steps. At first the elements are integrated over the spherical coordinates for all $\boldsymbol{R}_i$ points of a uniformly distributed 3D grid for the center-of-mass coordinates $\boldsymbol{R}$. To this end, the potential energy function is represented as an expansion in terms of the spherical harmonics at each grid point $\boldsymbol{R}_i$:

$$V(\boldsymbol{R}_i, \theta, \varphi) = \sum_{l=0}^{6} \sum_{m=-l}^{l} g_{lm}(\boldsymbol{R}_i) Y_l^m(\theta, \varphi)\,, \tag{3}$$

and thus they can be integrated analytically. The subsequent steps of the calculation are carried out by discrete Fourier transformations.

The 3D grid contained $20 \times 20 \times 20$ points, the cut-off energy for plane wave basis set was set to 7000 cm^{-1}, and $l \leq 7$ in expansion (2). These values provided good convergence of the eigenvalues in the energy region considered. The Hamiltonian matrix diagonalization was carried out using the Intel® Math Kernel Library.

The calculated rotational term values of an H_2 molecule in single-crystal silicon are listed in Table 1 for the ground translational state (in which the entire molecule carries out zero-point oscillations about the T site). One sees that these results are in good agreement with the previous 2D calculations [15] and experimental data [16]. The states obtained by solving the rotational problem were symmetry labeled in the O_h point group, and those obtained in translational-rotational calculations were labeled in the T_d point group. The column of Table 1 labeled $B_0l(l+1)$ contains the rotational energies of the molecule in the rigid rotor approximation. All energy values are given relative to the corresponding zero point energy.

For $l < 2$ the term values obtained for different models agree to within about 2 cm^{-1}; due to the system symmetry they remain degenerate even when the interaction of H_2 with the crystal is taken into account. The degeneracy is removed for the states with $l \geq 2$, where the splitting of energy levels for the 5D model is distinctly less than for the 2D model. It turns out that the translational-rotational interaction influences significantly the system properties and smoothes the effect of the rotational barrier for the low-lying states. On the whole, as one should expect, the results obtained with the most advanced model considered in this work are in best agreement with the experimental values [16].

CONCLUSIONS

The concepts of the project ATOMSK have been briefly reported. The project aims at developing a general approach to the modeling of free and localized polyatomic systems and involves the development of theoretical models and appropriate computational tools. The basic physical principles and the general scheme of the approach have been stated. The theory, the implementation of the models, and the methods under development are based on classical and/or quantum-mechanical (depending on the scale and properties of the system) descriptions of the objects under study.

The application of the general principles and the elements of the approach were exemplified for the H_2–Si system. Within the framework of the 5D model described above, the energy spectrum of molecular hydrogen in single-crystal silicon was calculated. It was seen that the translational-rotational interaction affects significantly the system properties; it weakens noticeably the effect of the rotational barrier for the low-lying states. The results obtained are in good agreement with the available experimental data.

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