INVERSE PROBLEMS IN ATOMIC AND MOLECULAR PHYSICS

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ABSTRACT

Methods for the parameter identification through the inverse analysis, apart of engineering and technology, are also important in other areas of science. In particular, methods based on the inverse analysis support theoretical models derived from quantum mechanics and usually labeled as "Quantum Chemistry", "Computational Chemistry" or "Many-body Problem". To this class belong methods aimed at the determination of the potentials describing interactions between molecular fragments. In the *direct* approach the potentials are derived from *ab initio* calculations aimed at solving the corresponding Schrödinger equation. In the *inverse* methods the form of the interaction potentials is deduced from the experimental data. The classical RKR method, developed by Rydberg, Klein and Rees more than half a century ago [1], became a most powerful tool for the determination of the bound-state potentials from the spectroscopic data. Over the decades, the idea of the inversion of the quantities directly derived from the experimental data (as, for example, the Franck-Condon factors) so that the results of the inversion procedure describe the interaction potentials has been transformed to a highly precise and mathematically sophisticated tool for probing the *ab initio* potentials. An example of a recent development and more references to other works may be found in ref. [2].

Another group of inverse problems relevant in theory of atomic and molecular spectra are based on the construction and solution of the inverse eigenvalue problems of large matrices in which matrix elements depend on some unknown parameters and some of the eigenvalues can be measured experimentally. In the *direct* approach atomic and molecular spectra may be approximated by spectra of Hermitian matrices representing the pertinent Hamiltonian operators in properly defined model spaces. However, for systems containing more than several (say 10) electrons the errors resulting from unavoidable approximations are usually large. A refinement of the results may be obtained using the *inverse* approach, in which some integrals (referred to as radial parameters) are determined from experimental data by solving a specific form of an inverse eigenvalue problem. The method proved to be very practical [3] and numerous modes of its implementation in both atomic [4] and molecular [5] spectroscopy may be found in the literature. The computations are supported by formal developments directed toward understanding the relations between the structure of the parameter space and the eigenvalue spectrum [5,6].

In this presentation the methods based on solutions of the inverse problems for the determination of parameters relevant to understanding atomic and molecular structure as, for example, methods for the determination of the radial parameters in the atomic spectroscopy, of the interaction integrals in the molecular spectroscopy, of the parameters defining molecular interaction potentials, are reviewed. Problems related to the symmetry assignment to specific energy levels and mathematical properties of the Hamiltonian matrices met in atomic and molecular physics [6] are also briefly discussed.

REFERENCES

[1]   R. Rydberg. *Z. Physik*, **73**, 376 (1931); O. Klein. *Z. Physik*, **76**, 1932; A. L. G. Rees, *Proc. Roy. Soc. Lon.*, **59**, 998, 1947.

[2]   O. Vallée, M. Soares and C. de Izarra Gremi. "A quantum method for the inversion of bound-free Franck-Condon factors", *J. Phys. B: At. Mol. Opt. Phys.*, **30**, L39-L45, 1997.

[3]   S. Fraga, J. Karwowski and K. M. S. Saxena. *Atomic energy levels*, Physical Sciences Data, Vol. 4, Elsevier, Amsterdam 1979.

[4]   A. S. Deakin and T. M. Luke. "On the inverse eigenvalue problem for matrices", *J. Phys. A: Math. Gen.*, **25**, 633-648, 1992.

[5]   J. Karwowski. "Assignment of the Electronic Transitions in Benzene" *J. Mol. Structure*, **19**, 143-166, 1973.

[6]   J. Karwowski. "Some properties of configuration interaction matrices and their applications", *J. Mol. Structure (Theochem)*, **537**, 9-15, 2001.