Preface

Level crossings/anticrossings are fundamental in quantum mechanics. In its two-level form, the problem is very simple. The two states have energies which are functions of a parameter γ. For some reference value γ_0 of the parameter, the separation in energy takes some relatively large value ΔE_0. At γ_0, the Hamiltonian eigenfunctions are ψ_{0a} and ψ_{0b}. As γ is increased, the energy difference ΔE decreases. When γ reaches its crossing value γ_c, this energy difference takes on a value ΔE_c whose magnitude is a minimum. If the Hamiltonian matrix is still diagonal in the γ_0-basis, a level crossing occurs: ΔE_c is zero. On the other hand, if the eigenfunctions ψ_{0a} and ψ_{0b} are coupled at γ_c, an avoided crossing takes place with ΔE_c being equal to twice the modulus of the coupling matrix element. If the derivatives of the energies with respect to γ are known outside the neighbourhood of the crossing, then the system can be characterized by measuring only two quantities: $(\gamma_c - \gamma_0)$ and ΔE_c.

In spite of its simplicity, a large variety of important problems can be reduced to this form. This Special Issue of Chemical Physics contains some representative investigations in molecular physics and in condensed matter physics. The transitions studied range in frequency from ~ 45000 cm^{-1} in the ultraviolet down to ~ 100 kHz in the low rf range. Many diverse experimental methods are discussed. Among the papers on molecular spectroscopy, these techniques include resonance-enhanced multiphoton ionization, laser-induced fluorescence, intermodulated fluorescence, Zeeman quantum beats, laser-Stark spectroscopy, laser magnetic resonance, microwave absorption, and molecular beam electric resonance. Among the papers on condensed matter, the techniques discussed include optical detection of electron spin resonance, nuclear magnetic resonance, and muon spin resonance. On the theoretical side, a molecular study discusses ab initio calculations using multi-reference configuration wave functions, while a condensed matter investigation applies the Liouville formalism to spin relaxation. In spite of the diversity in the methods used and in the systems studied, all of the papers involve level crossings and/or anticrossings that can be discussed in terms of the simple two-level problem outlined above.

The level crossing/anticrossing problems presented fall into one of two categories distinguished by the nature of the parameter γ. In what might be called the "external" case, γ is a laboratory electric or magnetic field. The Stark or Zeeman energy is varied until its difference for the two states involved cancels the corresponding zero-field energy difference. In what might be called the "internal" case, γ is a quantum number or a molecular property such as a bond length. In a typical quantum number case, there are two types of energy involved with different dependencies on γ such that the two energy differences cancel at γ_c.

Although a variety of problems is discussed here, this collection is not intended to be a comprehensive introduction to the application of level crossings/anticrossings. Many different types of studies could have been added if sufficient time and space were available. Rather, the purpose of the current issue is to present a sampling of the diverse areas in which level crossings/anticrossings arise, and to remind ourselves that common physical principles often underlie problems that on the surface seem very different.

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