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New Trends in Quantum Systems in Chemistry and Physics

Volume 2

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NEW TRENDS IN QUANTUM SYSTEMS IN CHEMISTRY AND PHYSICS

Progress in Theoretical Chemistry and Physics

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The titles published in this series are listed at the end of this volume.

Progress in Theoretical Chemistry and Physics

A series reporting advances in theoretical molecular and material sciences, including theoretical, mathematical and computational chemistry, physical chemistry and chemical physics

Aim and Scope

Science progresses by a symbiotic interaction between theory and experiment: theory is used to interpret experimental results and may suggest new experiments; experiment helps to test theoretical predictions and may lead to improved theories. Theoretical Chemistry (including Physical Chemistry and Chemical Physics) provides the conceptual and technical background and apparatus for the rationalisation of phenomena in the chemical sciences. It is, therefore, a wide ranging subject, reflecting the diversity of molecular and related species and processes arising in chemical systems. The book series *Progress in Theoretical Chemistry and Physics* aims to report advances in methods and applications in this extended domain. It will comprise monographs as well as collections of papers on particular themes, which may arise from proceedings of symposia or invited papers on specific topics as well as initiatives from authors or translations.

The basic theories of physics – classical mechanics and electromagnetism, relativity theory, quantum mechanics, statistical mechanics, quantum electrodynamics – support the theoretical apparatus which is used in molecular sciences. Quantum mechanics plays a particular role in theoretical chemistry, providing the basis for the valence theories which allow to interpret the structure of molecules and for the spectroscopic models employed in the determination of structural information from spectral patterns. Indeed, Quantum Chemistry often appears synonymous with Theoretical Chemistry: it will, therefore, constitute a major part of this book series. However, the scope of the series will also include other areas of theoretical chemistry, such as mathematical chemistry (which involves the use of algebra and topology in the analysis of molecular structures and reactions); molecular mechanics, molecular dynamics and chemical thermodynamics, which play an important role in rationalizing the geometric and electronic structures of molecular assemblies and polymers, clusters and crystals; surface, interface, solvent and solid-state effects; excited-state dynamics, reactive collisions, and chemical reactions.

Recent decades have seen the emergence of a novel approach to scientific research, based on the exploitation of fast electronic digital computers. Computation provides a method of investigation which transcends the traditional division between theory and experiment. Computer-assisted simulation and design may afford a solution to complex problems which would otherwise be intractable to theoretical analysis, and may also provide a viable alternative to difficult or costly laboratory experiments. Though stemming from Theoretical Chemistry, Computational Chemistry is a field of research

in its own right, which can help to test theoretical predictions and may also suggest improved theories.

The field of theoretical molecular sciences ranges from fundamental physical questions relevant to the molecular concept, through the statics and dynamics of isolated molecules, aggregates and materials, molecular properties and interactions, and the role of molecules in the biological sciences. Therefore, it involves the physical basis for geometric and electronic structure, states of aggregation, physical and chemical transformations, thermodynamic and kinetic properties, as well as unusual properties such as extreme flexibility or strong relativistic or quantum-field effects, extreme conditions such as intense radiation fields or interaction with the continuum, and the specificity of biochemical reactions.

Theoretical chemistry has an applied branch – a part of molecular engineering, which involves the investigation of structure–property relationships aiming at the design, synthesis and application of molecules and materials endowed with specific functions, now in demand in such areas as molecular electronics, drug design or genetic engineering. Relevant properties include conductivity (normal, semi- and supra-), magnetism (ferro- or ferri-), optoelectronic effects (involving nonlinear response), photochromism and photoreactivity, radiation and thermal resistance, molecular recognition and information processing, and biological and pharmaceutical activities, as well as properties favouring self-assembling mechanisms and combination properties needed in multifunctional systems.

Progress in Theoretical Chemistry and Physics is made at different rates in these various research fields. The aim of this book series is to provide timely and in-depth coverage of selected topics and broad-ranging yet detailed analysis of contemporary theories and their applications. The series will be of primary interest to those whose research is directly concerned with the development and application of theoretical approaches in the chemical sciences. It will provide up-to-date reports on theoretical methods for the chemist, thermodynamician or spectroscopist, the atomic, molecular or cluster physicist, and the biochemist or molecular biologist who wish to employ techniques developed in theoretical, mathematical or computational chemistry in their research programmes. It is also intended to provide the graduate student with a readily accessible documentation on various branches of theoretical chemistry, physical chemistry and chemical physics.

Preface

These two volumes collect thirty-eight selected papers from the scientific contributions presented at the Fourth European Workshop on *Quantum Systems in Chemistry and Physics* (QSCP-IV), held in Marly-le-Roi (France) in April 22-27, 1999. A total of one hundred and fifteen scientists attended the workshop, 99 from Europe and 16 from the rest of the world. They discussed the state of the art, new trends, and future evolution of the methods and applications.

The workshop was held in the old town of Marly-le-Roi, which lies to the West of Paris between the historic centres of Saint-Germain-en-Laye and Versailles. Participants were housed at the National Youth Institute, where over sixty lectures were given by leading members of the scientific community; in addition, over sixty posters were presented in two very animated sessions. We are grateful to the oral speakers and to the poster presenters for making the workshop such an stimulating experience. The social programme was also memorable - and not just for the closing banquet, which was held at the French Senate House. We are sure that participants will long remember their visit to the 'Musée des Antiquités Nationales': created by Napoleon III at the birthplace of Louis XIV, this museum boasts one of the world finest collections of archeological artifacts.

The Marly-le-Roi workshop followed the format established at the three previous meetings, organized by Prof. Roy McWeeny at San Miniato Monastery, Pisa (Italy) in April, 1996 (the proceedings of which were published in the Kluwer TMOE series); Dr Steve Wilson at Jesus College, Oxford (United Kingdom) in April, 1997 (which resulted in two volumes in Adv. Quant. Chem.); and Prof. Alfonso Hernandez-Laguna at Los Alixares Hotel, Granada (Spain) in April, 1998 (for which proceedings appeared in the present series). These meetings, sponsored by the European Union in the frame of the Cooperation in Science and Technology (COST) chemistry actions, create a forum for discussion, exchange of ideas and collaboration on innovative theory and applications.

Quantum Systems in Chemistry and Physics encompasses a broad spectrum of research where scientists of different backgrounds and interests jointly place special emphasis on quantum theory applied to molecules, molecular interactions and materials. The meeting was divided into several sessions, each addressing a different aspect of the field: 1 - Density matrices and density functionals; 2 - Electron correlation treatments; 3 - Relativistic formulations and effects; 4 - Valence theory (chemical bond and bond breaking); 5 - Nuclear motion (vibronic effects and flexible molecules); 6 - Response theory (properties and spectra); 7 - Reactive collisions and chemical reactions, computational chemistry and physics; and 8 - Condensed matter (clusters and crystals, surfaces and interfaces).

Density matrices and density functionals have important roles in both the interpretation and the calculation of atomic and molecular structures and properties. The fundamental importance of electronic correlation in many-body systems makes this topic a central area of research in quantum chemistry and molecular physics. Relativistic effects are being increasingly recognized as an essential ingredient of studies on many-body systems, not only from a formal viewpoint but also for practical applications to molecules and materials involving heavy atoms. Valence theory deserves special attention since it

improves the electronic description of molecular systems and reactions from the point of view used by most laboratory chemists. Nuclear motion constitutes a broad research field of great importance accounting for the internal molecular dynamics and spectroscopic properties.

Also very broad and of great importance in physics and chemistry is the topic of response theory, where electric and magnetic fields interact with matter. The study of chemical reactions and collisions is the cornerstone of chemistry, where traditional concepts like potential-energy surfaces or transition complexes appear to become insufficient, and the new field of computational chemistry finds its main applications. Condensed matter is a field in which progressive studies are performed, from few-atom clusters to crystals, surfaces and materials.

We are pleased to acknowledge the support given to the Marly-le-Roi workshop by the European Commission, the Centre National de la Recherche Scientifique (CNRS) and Université Pierre et Marie Curie (UPMC). We would like to thank Prof. Alfred Maquet, Director of Laboratoire de Chimie Physique in Paris, Prof. Alain Sevin, Director of Laboratoire de Chimie Théorique in Paris, and Dr Gérard Rivière, Secretary of COST-Chemistry in Brussels, for financial and logistic help and advice. Prof. Gaston Berthier, Honorary Director of Research, and Prof. Raymond Daudel, President of the European Academy, gave the opening and closing speeches. The supportive help of Ms Françoise Debock, Manager of INJEP in Marly-le-Roi, is also gratefully acknowledged. Finally, it is a pleasure to thank the work and dedication of all other members of the local organizing team, especially Alexandre Kuleff, Alexis Markovits, Cyril Martinsky and, last but not least, Ms Yvette Masseguin, technical manager of the workshop.

Jean Maruani and Christian Minot
Paris, 2000

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Response Theory: Properties and Spectra

ON GAUGE INVARIANCE AND MOLECULAR ELECTRODYNAMICS

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Abstract. A general account of the interaction of electric charges with electromagnetic radiation is presented, the charges being treated in the non-relativistic approximation. The two main approaches in the literature, based on either the potentials of the electromagnetic field (`minimal coupling´) or the polarization fields of the charges (e.g., the `multipolar Hamiltonian´) are presented in a unified framework, that characterizes them as simply different viewpoints of the same general structure. This structure is very suitable for a discussion of the gauge invariance of the theory. The final quantum mechanical Hamiltonian presented here has recently been shown to provide the basis for a proof of the gauge invariance of its associated S-matrix to all orders of perturbation theory, provided the S-matrix is taken on the energy-shell. Some outstanding problems are described briefly.

1. Introduction

The quantum theory of atoms and molecules interacting with electromagnetic radiation has a very long history; it was the subject of the first successful attempts at field quantization in the late 1920's. It has been presented in a variety of ways of which only two have become well-known. Firstly, there is the `minimal coupling´ form using a vector potential for the radiation, generally subject to the Coulomb gauge condition. There is also the `multipolar Hamiltonian´ in which electric and magnetic multipole moments are coupled directly to the (transverse) electric and magnetic fields. This latter form can be generalized by replacing the multipole series by closed form `polarization fields´, and when this is done one sees that the polarization fields are subject to the same kind of arbitrariness as that implied by the gauge transformations of the vector potential. Some definite choice of vector potential, or of the polarization fields, has always seemed necessary in order to have a practical scheme for calculations of absorption, emission and scattering phenomena; it is thus crucial to decide what calculations can be made that are independent of the choices made

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for the gauge (or the polarization fields), and for this one needs a suitably general theory.

In covariant QED gauge invariance is a straightforward matter; the field potential A_μ occurs coupled linearly to the 4-current j^μ which satisfies the equation of continuity $\nabla_\mu j^\mu = 0$, and this means that the gauge transformations of the potential are easily disposed of. It is therefore perhaps worth noting explicitly at the outset why there is something to discuss for the non-relativistic theory. The point is simply that in molecular electrodynamics we do *not* calculate with the covariant formalism and take the non-relativistic limit at the end. Instead we start again with the atomic/molecular Hamiltonian (a collection of a fixed number of charges) and the Hamiltonian for free radiation which are coupled by a gauge-dependent interaction. The complete Hamiltonian is easily shown to be gauge invariant; furthermore the equation of continuity must still be satisfied but it does not seem possible to use it straightforwardly as in covariant QED to show that perturbation theory is gauge invariant, and as we shall see there are examples in the literature of gauge-dependent perturbation calculations (e.g., of spectral lineshapes).

This paper presents an account of the dynamics of electric charges coupled to electromagnetic fields. The main approximation is to use non-relativistic forms for the charge and current density. A quantum theory requires either a Lagrangian or a Hamiltonian formulation of the dynamics; in atomic and molecular physics the latter is almost universal so the main thrust of the paper is the development of a general Hamiltonian. It is this Hamiltonian that provides the basis for a recent demonstration that the S-matrix on the energy shell is gauge-invariant to all orders of perturbation theory.

2. Charges, currents and polarization fields

In electrodynamics the coupling between matter and the electromagnetic field is mediated by the charge density, $\rho(\mathbf{x},t)$, and the current density, $\mathbf{j}(\mathbf{x},t)$, which together satisfy an equation of continuity,

$$\frac{d\rho(x,t)}{dt} + \Delta . j(x,t) = 0 , \tag{1}$$

that expresses local conservation of charge. In the electrodynamics of bulk matter it is usual to express the charge and current density in terms of two *polarization* fields. In the classical formulation of Lorentz [1] this description has a definite physical motivation, being accompanied by an explicit division of the charges into 'bound' and 'free' charge densities. But we shall not make any assumptions here about localization; thus we write

$$\rho(x,t) = - \Delta . P(x,t) \tag{2a}$$

$$j(x,t) = \frac{dP(x,t)}{dt} + \Delta \wedge M(x,t) \tag{2b}$$

with $\rho(\mathbf{x},t)$ being the *total* charge density. Equation (2) is to be taken to apply to a single charge, and then extended by linearity to a collection of N charges. These are classical equations which eventually will have to be reinterpreted as operator relations for a quantum theory; the polarization fields will become operators, because $\rho(\mathbf{x},t)$ and $\mathbf{j}(\mathbf{x},t)$ do. We retain the classical terminology however; thus $\mathbf{P}(\mathbf{x},t)$ and $\mathbf{M}(\mathbf{x},t)$ are called the electric polarization and magnetic polarization (`magnetization') fields respectively. Such a polarization field description has commonly been regarded as being particularly `physical' or `natural' (e.g. through its multipolar representation) even though the pair $\{\mathbf{P}, \mathbf{M}\}$ are not defined uniquely by (2) [2]. It should be noted that *in a quantum theory* the distinction between `bound' and `free' charges is one that is carried by the solutions of the Schrödinger equation for the charges (bound-state versus continuum wavefunctions) and is not directly associated with the operators in the Schrödinger representation we anticipate using in atomic and molecular physics.

To begin with we concentrate on equation (2a), which is purely static. We define the Green's function $\mathbf{g}(\mathbf{x},\mathbf{x}')$ for the divergence operator:

$$\Delta_x . g(x,x') = - \delta^3(x - x'), \tag{3}$$

in terms of which a formal solution of (2a) is

$$P(x,t) = \int d^{3'}x\, g(x,x')\rho(x',t). \tag{4}$$

Here $\rho(\mathbf{x},t)$ for point charges can be expressed as a sum of Dirac delta functions in the usual way. The *longitudinal* component of $\mathbf{g}$ is well-defined; it can be written as [3]:

$$\mathbf{g}(\mathbf{x},\mathbf{x}')^{\parallel} = \nabla_{\mathbf{x}} \frac{1}{4\pi|\mathbf{x}-\mathbf{x}'|}. \tag{5}$$

Although the differential equation (3) is consistent with solutions involving $(\mathbf{x} - \mathbf{x}')$, these are only a subset of the solution set, so treating $\mathbf{x}$ and $\mathbf{x}'$ as separate variables, its Fourier transform on $\mathbf{x}$ yields the longitudinal solution

$$\mathbf{g}(\mathbf{p},\mathbf{x}')^{\parallel} = -\frac{i\mathbf{p}}{p^2} e^{i\mathbf{p}.\mathbf{x}'}. \tag{6}$$

The longitudinal component of $\mathbf{g}(\mathbf{p},\mathbf{x}')$is directed along $\mathbf{p}$ so we introduce an orthogonal triad of unit vectors $\{\varepsilon_i,\ i = 1,2,3\}$ with $\varepsilon_3 = \mathbf{p}/p$; then the transverse component lies in the plane containing $\{\varepsilon_1,\varepsilon_2\}$,

$$g(p,x')^{\perp} = \varepsilon_1 f(p,x') + \varepsilon_2 h(p,x'), \tag{7}$$

in terms of two scalar functions f and h. Since $\mathbf{g}(\mathbf{p},\mathbf{x}')^{\perp}$ satisfies

$$p\ \varepsilon_3 \cdot g(p,x')^{\perp} = 0 \tag{8}$$

$f(\mathbf{p},\mathbf{x}')$ and $h(\mathbf{p},\mathbf{x}')$ can behave as p^{ν}, $\nu \geq -1$ near $p = 0$; otherwise their singularities are controlled only by the requirement that the Fourier transforms required for (2) exist. The transverse component of the Green's function $\mathbf{g}(\mathbf{x},\mathbf{x}')$ is thus essentially arbitrary. In view of (4) these characteristics are inherited by the longitudinal and transverse components of the electric polarization field, $\mathbf{P}(\mathbf{x},t)$ (and its transform $\mathbf{P}(\mathbf{p},t)$). We note specifically that the 'long-wavelength' limit, $\mathbf{p} \to 0$, of $\mathbf{P}(\mathbf{p},t)$ need not exist. A general account of the use of polarization fields in electrodynamics should reflect this situation which may strongly constrain any proposed physical interpretation.

Given a particular choice of electric polarization field, $\mathbf{P}(\mathbf{x},t)$, we can use it to solve for $\mathbf{M}(\mathbf{x},t)$ in (2b). If $\mathbf{j}(\mathbf{x},t)$ and $\mathbf{P}(\mathbf{x},t)$ are separated into longitudinal and transverse parts, a simple calculation shows that the longitudinal contributions cancel identically because of the equation of continuity, (1). We then find,

$$\begin{aligned} M(x,t) = \int d^3x' \frac{1}{4\pi |x - x'|} (\Delta' \wedge j(x',t) \\ - \int d^3x''\ \Delta' \wedge g(x',x'')\ \frac{d\rho(x'',t)}{dt}). \end{aligned} \tag{9}$$

Equations (4) and (9) are general forms for the polarization fields which display their arbitrary content through their dependence on the Green's function $\mathbf{g}(\mathbf{x},\mathbf{x}')$.

3. Electrodynamics in Lagrangian form

A Lagrangian for a collection of charged particles in an electromagnetic field can be written down directly using the polarization fields

$$L = L_p + \int d^3x\, P(x,t).E(x,t) + \int d^3x\, M(x,t).B(x,t), \tag{10}$$