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Advances in Quantum Methods and Applications in Chemistry, Physics, and Biology

Springer

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Progress in Theoretical Chemistry and Physics

VOLUME 27

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ISSN 1567-7354 Progress in Theoretical Chemistry and Physics
ISBN 978-3-319-01528-6 ISBN 978-3-319-01529-3 (eBook)
DOI 10.1007/978-3-319-01529-3
Springer Cham Heidelberg New York Dordrecht London

Library of Congress Control Number: 2013950105

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PTCP Aim and Scope

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 and biophysics.*

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 from 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, to 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 super-), magnetism (ferro- and ferri-), optoelectronic effects (involving nonlinear response), photochromism and photoreactivity, radiation and thermal resistance, molecular recognition and information processing, 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 and computational chemistry in their research programs. 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

This volume collects 20 selected papers from the scientific contributions presented at the Seventeenth International Workshop on Quantum Systems in Chemistry and Physics (and Biology), QSCP-XVII, which was organized by Prof. Matti Hotokka at Åbo Akademi University, Turku, Finland, from August 19 to 25, 2012. Over 120 scientists from 27 countries attended this meeting. Participants of the QSCP-XVII workshop discussed the state of the art, new trends, and future evolution of methods in molecular quantum mechanics, as well as their applications to a wide variety of problems in chemistry, physics, and biology.

The large attendance attained in this conference was particularly gratifying. It is the renowned interdisciplinary character and friendly atmosphere of QSCP meetings that makes them so successful discussion forums.

Turku is located in the southwestern part of Finland. It was the capital city of the country as well as its religious and cultural center throughout the Swedish period. Christina, Queen of Sweden, founded the Åbo Akademi University in Turku in 1630. When Finland became a Grand Duchy under Alexander I, Czar of Russia, in 1809, the former University was transferred to the new capital, Helsinki, and eventually became the University of Helsinki.

The present-day Åbo Akademi University was founded in 1918, shortly after Finland became independent from Russia. Some of the buildings of the old Åbo Akademi University, such as the Ceremonial Hall, are still used by the University. Today, Turku is the seat of the Archbishop of Finland and an active cultural and industrial city endowed with numerous museums, art galleries and historical sites, as well as an important seaport.

Details of the Turku meeting, including the scientific program, can be found on the web site: http://www.qscp17.fi. Altogether, there were 19 morning and afternoon sessions, where 56 plenary talks were given, and one evening poster session, with 21 flash presentations for a total of 55 posters displayed. We are grateful to all participants for making the QSCP-XVII workshop such a stimulating experience and great success.

QSCP-XVII followed the traditions established at previous workshops:
QSCP-I, organized by Roy McWeeny in 1996 at San Miniato (Pisa, Italy);

QSCP-II, by Stephen Wilson in 1997 at Oxford (England);
QSCP-III, by Alfonso Hernandez-Laguna in 1998 at Granada (Spain);
QSCP-IV, by Jean Maruani in 1999 at Marly-le-Roi (Paris, France);
QSCP-V, by Erkki Brändas in 2000 at Uppsala (Sweden);
QSCP-VI, by Alia Tadjer in 2001 at Sofia (Bulgaria);
QSCP-VII, by Ivan Hubac in 2002 near Bratislava (Slovakia);
QSCP-VIII, by Aristides Mavridis in 2003 at Spetses (Athens, Greece);
QSCP-IX, by Jean-Pierre Julien in 2004 at Les Houches (Grenoble, France);
QSCP-X, by Souad Lahmar in 2005 at Carthage (Tunisia);
QSCP-XI, by Oleg Vasyutinskii in 2006 at Pushkin (St Petersburg, Russia);
QSCP-XII, by Stephen Wilson in 2007 near Windsor (London, England);
QSCP-XIII, by Piotr Piecuch in 2008 at East Lansing (Michigan, USA);
QSCP-XIV, by Gerardo Delgado-Barrio in 2009 at El Escorial (Madrid, Spain);
QSCP-XV, by Philip Hoggan in 2010 at Cambridge (England);
QSCP-XVI, by Kiyoshi Nishikawa in 2011 at Kanazawa (Japan).

The lectures presented at QSCP-XVII were grouped into nine areas in the field of *Quantum Systems in Chemistry, Physics, and Biology*, ranging from Concepts and Methods in Quantum Chemistry and Physics through Molecular Structure and Dynamics, Reactive Collisions, and Chemical Reactions, to Computational Chemistry, Physics, and Biology.

The width and depth of the topics discussed at QSCP-XVII are reflected in the contents of this volume of proceedings in the book series *Progress in Theoretical Chemistry and Physics*, which includes four sections:

I. Fundamental Theory (4 papers);
II. Molecular Structure, Properties and Processes (5 papers);
III. Clusters and Condensed Matter (9 papers);
IV. Structure and Processes in Biosystems (2 papers).

In addition to the scientific program, the workshop had its usual share of cultural events. There was an entertaining concert by a tuba orchestra on the premises. The City of Turku hosted a reception on the museum sail ship Suomen Joutsen, and one afternoon was devoted to a visit to the archipelago on board of the old-fashioned steamship Ukkopekka. The award ceremony of the CMOA Prize and Medal took place in the historical Ceremonial Hall of the old Åbo Akademi University.

The CMOA Prize was shared between two selected nominees: Marcus Lundberg (Uppsala, Sweden) and Adam Wasserman (Purdue, USA). The CMOA Medal was awarded to Pr. Martin Quack (ETH, Switzerland). Following an established custom at QSCP meetings, the venue of the next (XVIIIth) workshop was disclosed at the end of the banquet: Paraty (Rio de Janeiro), Brazil, in December 2013.

We are pleased to acknowledge the generous support given to the QSCP-XVII conference by the Federation of Finnish Learned Societies, the Svenska Tekniska Vetenskaps-Akademien i Finland, the City of Turku, the Åbo Akademi University, the Walki company, and Turku Science Park. We are most grateful to the members of the Local Organizing Committee (LOC) for their work and dedication, which made the stay and work of the participants both pleasant and fruitful. Finally, we would like to thank the members of the International Scientific Committee (ISC) and Honorary Committee (HC) for their invaluable expertise and advice.

We hope the readers will find as much interest in consulting these proceedings as the participants in attending the meeting.

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Contents

Part I Fundamental Theory

Part II Molecular Structure, Properties and Processes

Part III Clusters and Condensed Matter

Part IV Structure and Processes in Biosystems

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Part I
Fundamental Theory

Chapter 1
The Potential Energy Surface in Molecular Quantum Mechanics

Brian Sutcliffe and R. Guy Woolley

Abstract The idea of a Potential Energy Surface (PES) forms the basis of almost all accounts of the mechanisms of chemical reactions, and much of theoretical molecular spectroscopy. It is assumed that, in principle, the PES can be calculated by means of clamped-nuclei electronic structure calculations based upon the Schrödinger Coulomb Hamiltonian. This article is devoted to a discussion of the origin of the idea, its development in the context of the Old Quantum Theory, and its present status in the quantum mechanics of molecules. It is argued that its present status must be regarded as uncertain.

1.1 Introduction

> The Coulombic Hamiltonian H' does not provide much obvious information or guidance, since there is [*sic*] no specific assignments of the electrons occurring in the systems to the atomic nuclei involved—hence there are no atoms, isomers, conformations etc. In particular one sees no *molecular symmetry*, and one may even wonder where it comes from. Still it is evident that all of this information must be contained somehow in the Coulombic Hamiltonian H' [1].
>
> Per-Olov Löwdin, Pure. Appl. Chem. **61**, 2071 (1989)

This paper addresses the question Löwdin wondered about in terms of what quantum mechanics has to say about molecules. A conventional chemical description of a stable molecule is a collection of atoms held in a semi-rigid arrangement by chemical bonds, which is summarized as a molecular structure. Whatever 'chemical bonds' might be physically, it is natural to interpret this statement in terms of bonding forces which are conservative. Hence a stable molecule can be associated with a *potential energy* function that has a minimum value below the energy of all the clusters that the molecule can be decomposed into. Finding out about these forces, or equivalently the associated potential energy, has been a major activity for the past century. There is no *a priori* specification of *atomic* interactions from basic physical laws so the approach has been necessarily indirect.

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M. Hotokka et al. (eds.), *Advances in Quantum Methods and Applications in Chemistry, Physics, and Biology*, Progress in Theoretical Chemistry and Physics 27,
DOI 10.1007/978-3-319-01529-3_1,

After the discovery of the electron [2] and the triumph of the atomic, mechanistic view of the constitution of matter, it became universally accepted that any specific molecule consists of a certain number of electrons and nuclei in accordance with its chemical formula. This can be translated into a microscopic model of point charged particles interacting through Coulomb's law with non-relativistic kinematics. These assumptions fix the molecular Hamiltonian as precisely what Löwdin referred to as the 'Coulombic Hamiltonian',

$$\mathsf{H} = \sum_{i}^{n} \frac{p_i^2}{2m_i} + \sum_{i<j}^{n} \frac{e_i e_j}{4\pi\varepsilon_0 |\mathbf{q}_i - \mathbf{q}_j|} \tag{1.1}$$

where the n particles are described by empirical charge and mass parameters $\{e_i, m_i, i = 1, \ldots, n\}$, and Hamiltonian canonical variables $\{\mathbf{q}_i, \mathbf{p}_i, i = 1, \ldots, n\}$, which after quantization are regarded as non-commuting operators.

As is well-known classical dynamics based on (1.1) fails completely to account for the stability of atoms and molecules, as evidenced through the facts of chemistry and spectroscopy. And so, starting about a century ago, there was a progressive modification of dynamics as applied to the microscopic world from classical ('rational') mechanics, through the years of the Old Quantum Theory until finally quantum mechanics was defined. This slow evolution left its mark on the development of molecular theory in as much that classical ideas survive in modern Quantum Chemistry. In the following sections we review some aspects of this progression; we also emphasize that a direct approach to a quantum theory of a molecule can be based on the quantized version of (1.1), simply as an extension of the highly successful quantum theory of the atom.

It is of interest to compare this so-called 'Isolated Molecule' model with the conventional account; after all, the sentiment of the quotation from Löwdin reflects the widespread view that the model is the fundamental basis of Quantum Chemistry. Even though there are no closed solutions for molecules, it is certainly possible to characterize important qualitative features of the solutions for the model because they are determined by the *form* of the defining equations [1, 3, 4]. One of the most important ideas in molecular theory is the Potential Energy Surface for a molecule; this is basic for theories of chemical reaction rates and for molecular spectroscopy. In Sect. 1.2 we discuss some aspects of its classical origins. Then in Sect. 1.3 we revisit the same topics from the standpoint of quantum mechanics, where we will see that if we eschew the conventional classical input (classical fixed nuclei), *there are no Potential Energy Surfaces* in the solutions derived from (1.1). It is *not* the case that the conventional approach via the clamped-nuclei Hamiltonian is merely a convenience that permits practical calculation (in modern terms, computation) with results concordant with the underlying Isolated Molecule model that would be obtained if only the computations could be done. On the contrary, a qualitative modification of the formalism is imposed by hand. The paper concludes in Sect. 1.4 with a discussion of these results; some relevant mathematical results are illustrated in the Appendix.

We wish to emphasize that the paper is about a difficult technical problem; it is not a contribution to the philosophy of science. In the traditional picture, (1.15) is widely held to be exact in principle, so if the adiabatic approximation is found to be inadequate we would expect to do 'better' by including coupling terms. Our analysis implies that belief is not well founded because (1.15) is not well founded *a priori* in quantum mechanics; it requires an extra ingredient put in by hand. It might work, or it might not; in other words it is not a sure-fire route to a better account. While we can't offer a better alternative, that information is surely important for chemical physics.

1.2 Classical Origins

The idea of a Potential Energy Surface can be glimpsed in the beginnings of chemical reaction rate theory that go beyond the purely thermodynamic considerations of van 't Hoff and Duhem more than a century ago, and in the first attempts to understand molecular ('band') spectra in dynamical terms in the same period. Thereafter progress was rapid as the newly emerging ideas of a 'quantum theory' were developed; by the time that quantum mechanics was finalized (1925/6) ideas about the separability of electronic and nuclear motions in molecules were common currency, and were carried forward into the new era. In this section we describe how this development took place.

1.2.1 Rates of Chemical Reactions—René Marcelin

The idea of basing a theory of chemical reactions (chemical dynamics) on an energy function that varies with the configurations of the participating molecules seems to be due to Marcelin. In his last published work, his thesis, [5], Marcelin showed how the Boltzmann distribution for a system in thermal equilibrium and statistical mechanics can be used to describe the rate, v, of a chemical reaction. The same work was republished in the Annales de Physique [6] shortly after his death.[1] The main conclusions of the thesis were summarized in two short notes published in Comptes Rendus in early 1914 [7, 8]. His fundamental result can be expressed, in modern terms, as

$$v = M\left(e^{-\Delta G_{+}^{\#}/RT} - e^{-\Delta G_{-}^{\#}/RT}\right) \tag{1.2}$$

where R is the molar gas constant, T is the temperature in Kelvin, the subscripts $+, -$ refer to the forward and reverse reactions, and $\Delta G^{\#}$ is the change in the molar Gibbs (free) energy in going from the initial $(+)$ or final $(-)$ state to the 'activated

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[1] René Marcelin was killed in action fighting for France in September 1914.

state'. The pre-exponential factor M is obtained formally from statistical mechanics. Marcelin gave several derivations of this result using both thermodynamic arguments and also the statistical mechanics he had learnt from Gibbs's famous memoir [9]. It is perhaps worth remarking that Gibbs saw statistical mechanics as the completion of Newtonian mechanics through its extension to conservative systems with an arbitrarily large, though finite, number of degrees of freedom. The laws of thermodynamics could easily be obtained from the principles of statistical mechanics, of which they were the incomplete expression, but Gibbs did not require thermodynamic systems to be made up of molecules; he explicitly did not wish his account of rational mechanics to be based on hypotheses concerning the constitution of matter, which at the time were still controversial [10].

From our point of view the most interesting aspect of Marcelin's account is the suggestion that molecules can have more degrees of freedom than those of simple point material particles. In this perspective, a molecule can be assigned a set of Lagrangian coordinates $\mathbf{q} = q_1, q_2, \dots, q_n$, and their corresponding canonical momenta $\mathbf{p} = p_1, p_2, \dots, p_n$. Then the instantaneous *state* of the molecule is associated with a 'representative' point in the canonical phase-space $\mathscr{P}$ of dimension $2n$, and so "as the position, speed or structure of the molecule changes, its representative point traces a trajectory in the $2n$-dimensional phase-space" [5].

In his phase-space representation of a chemical reaction the transformation of reactant molecules into product molecules was viewed in terms of the passage of a set of trajectories associated with the 'active' molecules through a 'critical surface' $\mathscr{S}$ in $\mathscr{P}$ that divides $\mathscr{P}$ into two parts, one part being associated with the reactants, the other with the products. Such a [hyper]surface is defined by a relation

$$S(\mathbf{q}, \mathbf{p}) = 0.$$

According to Marcelin, for passage through this surface it is required[2] [5]

> [une molécule] il faudra [...] qu'elle atteigne une certaine région de l'éspace sous une obliquité convenable, que sa vitesse dépasse une certain limite, que sa structure interne corresponde à une configuration instable, *etc.*; ...

In modern notation, the volume of a cell in the $2n$-dimensional phase-space is

$$d\varpi = d\mathbf{q}d\mathbf{p}.$$

The number of points in $d\varpi$ is given by the Gibbs distribution function f

$$d\nu = f(\mathbf{q}, \mathbf{p}, t)d\varpi. \tag{1.3}$$

Marcelin chose the distribution function for the active molecules as

$$f(\mathbf{q}, \mathbf{p}, t) = e^{-G^{\#}_{+}/RT} e^{-\mathscr{H}(\mathbf{q},\mathbf{p})/k_B T} \tag{1.4}$$

---

[2] That a molecule must reach a certain region of space at a suitable angle, that its speed must exceed a certain limit, that its internal structure must correspond to an unstable configuration *etc.*; ...

where k_B is Boltzmann's constant, $\mathscr{H}$ is the Hamiltonian function for the molecule, and $G_+^\#$ is the Gibb's free energy of the active molecules relative to the mean energy of the reactant molecules. It is independent of the canonical variables. There is an analogous expression for the reverse reaction involving $G_-^\#$. Marcelin quoted a formula due to Gibbs [9] for the number of molecules dN crossing a surface element ds in the critical surface in the neighbourhood of $\mathbf{q}, \mathbf{p}$, in time dt, which may be written in shorthand as

$$dN = dt f(\mathbf{q}, \mathbf{p}, t) J(\dot{\mathbf{q}}, \dot{\mathbf{p}}, \mathbf{q}, \mathbf{p})$$

where $\dot{\mathbf{p}}, \dot{\mathbf{q}}$ are regarded as functions of $\mathbf{q}, \mathbf{p}$ by virtue of Hamilton's equations of motion. The total rate is

$$v = \int d\varpi f(\mathbf{q}, \mathbf{p}) J \delta\big[S(\mathbf{q}, \mathbf{p})\big] \tag{1.5}$$

where the delta function confines the integration to the critical surface $\mathscr{S}$. Equation (1.2) results from taking the difference between this expression for the forward and reverse reactions, and factoring out the terms in $G_\pm^\#$; the remaining integration, which Marcelin did not evaluate, defines the multiplying factor M.

1.2.2 Molecular Spectroscopy and the Old Quantum Theory

Although the discussion in the previous section looks familiar, it does so only because of the modern interpretation we put upon it.[3] It is important to note that nowhere did Marcelin elaborate on how the canonical variables were to be chosen, nor even how n could be fixed in any given case. The words 'atom', 'electron', 'nucleus' do not appear anywhere in his thesis, in which respect he seems to have followed the scientific philosophy of his countryman Duhem [11]. On other pages in the thesis Marcelin referred to the 'structure' (also 'architecture') of a molecule and to molecular 'oscillations' but never otherwise invoked the atomic structural conception of a molecule due to e.g. van 't Hoff, although he was very well aware of van 't Hoff's Physical Chemistry.

Contemporary with Marcelin's investigation of chemical reaction rates was the introduction of a completely novel model of an atom due to Rutherford. However

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[3] Nevertheless it seems proper to regard Marcelin's introduction of phase-space variables and a critical reaction surface into chemical dynamics as the beginning of a formulation of the Transition State Theory that was developed by Wigner in the 1930's [12–15]. The $2n$ phase-space variables $\mathbf{q}, \mathbf{p}$ were identified with the *n nuclei* specified in the chemical formula of the participating species, and the Hamiltonian $\mathscr{H}$ was that for classical nuclear motion on a *Potential Energy Surface*; this dynamics was assumed to give rise to a critical surface which was such that reaction trajectories cross the surface precisely *once*. The classical nature of the formalism was quite clear because the Uncertainty Principle precludes the precise specification of position on the critical surface simultaneously with the momentum of the nuclei.

it quickly became apparent that Rutherford's solar system model of the atom (planetary electrons moving about a central nucleus) cannot avoid eventual collapse if classical electrodynamics applies to it. This is because of Earnshaw's theorem which states that it is impossible for a collection of charged particles to maintain a static equilibrium purely through electrostatic forces [16]. This is the classical result that Bohr alluded to in his 1922 Nobel lecture [17] to rule out an electrostatical explanation for the stability of atoms and molecules.

The theorem may be proved by demonstrating a contradiction. Suppose the charges are at rest and consider the motion of a particular charge e_n in the electric field, $\mathbf{E}$, generated by all of the other charged particles. Assume that this particular charge has $e_n > 0$. The equilibrium position of this particle is the point $\mathbf{x}_n^0$ where $\mathbf{E}(\mathbf{x}_n^0) = \mathbf{0}$, since the force on the charge is $e_n\mathbf{E}(\mathbf{x}_n)$ (the Lorentz force for this static case). Obviously, $\mathbf{x}_n^0$ cannot be the equilibrium position of any other particle. However, in order for $\mathbf{x}_n^0$ to be a stable equilibrium point, the particle must experience a restoring force when it is displaced from $\mathbf{x}_n^0$ in any direction. For a positively charged particle at $\mathbf{x}_n^0$, this requires that the electric field points radially towards $\mathbf{x}_n^0$ at all neighbouring points. But from Gauss's law applied to a small sphere centred on $\mathbf{x}_n^0$, this corresponds to a *negative* flux of $\mathbf{E}$ through the surface of the sphere, implying the presence of a *negative charge* at $\mathbf{x}_n^0$, contrary to our original assumption. Thus $\mathbf{E}$ cannot point radially towards $\mathbf{x}_n^0$ at all neighbouring points, that is, there must be some neighbouring points at which $\mathbf{E}$ is directed away from $\mathbf{x}_n^0$. Hence, a positively charged particle placed at $\mathbf{x}_n^0$ will always move towards such points. There is therefore no static equilibrium configuration. According to classical electrodynamics accelerated charges must radiate electromagnetic energy, and hence lose kinetic energy, so even a dynamical model cannot be stable according to purely classical theory.

Molecular models which can be represented in terms of the (phase-space) variables of classical dynamics had a far-reaching influence on the interpretation of molecular spectra after the dissemination of Bohr's quantum theory of atoms and molecules based on transitions between stationary states [18]. An important feature of his new theory was that classical electrodynamics should be deemed to be still operative when transitions took place, but *not* when the system was in a stationary state, by fiat. Bohr had originally used the fact that two particles with Coulombic interaction lead to a Hamiltonian problem that is completely soluble by separation of variables. With more particles and Coulombic interactions this is no longer true; however by largely qualitative reasoning he was able to develop a quantum theory of the atom and the Periodic Table (reviewed in [17]). Furthermore by the introduction of Planck's constant h through the angular momentum quantization condition, Bohr solved another problem of the classical theory. In classical electrodynamics the only characteristic length available is the classical radius r_o for a charged particle. This is obtained by equating the rest-mass energy for the charge to the electrostatic energy of a charged sphere of radius r_o

$$r_o = \left(\frac{e^2}{4\pi\varepsilon_0 mc^2}\right).$$

For an electron this yields $r_o \approx 2.8 \times 10^{-15}$ m and an even smaller value for any nucleus. It was clear that this was far too small to be relevant to an atomic theory; of course the Bohr radius $a_o \approx 0.5 \times 10^{-10}$ m is of just the right dimension.

Bohr's theory developed into the Old Quantum Theory which was based on a phase-space description of an atomic-molecular system and theoretical techniques originally developed in celestial mechanics. These came from the application of the developing quantum theory to molecular band spectra by Schwarzschild [19] and Heurlinger [20] who used it to describe the quantized vibrational and rotational energies of small molecules (diatomic and symmetric top structures). Schwarzschild, an astrophysicist, was responsible for the introduction of action-angle methods as a basis for quantization in atomic/molecular theory. Heurlinger assumed a quantization of the energy of the nuclear vibration analogous to that used by Planck for his ideal linear oscillators, with the possibility of anharmonic behaviour. Thus a force-law or *potential energy* depending on the separation of the nuclei, for a given arrangement of the electrons, was required.

The basic calculational tool was a perturbation theory approach developed enthusiastically by Born [21] and Sommerfeld [22] with their research assistants. The solution of the Hamiltonian equations of motion could be attempted via the Hamilton-Jacobi method based on canonical transformations of the action-angle variables. This leads to an expression for the energy that is a function of the action integrals only. The action (or 'phase') integrals are constants of the motion, and are also adiabatic invariants [23], and as such are natural objects for quantization according to the 'quantum conditions'. Thus for a separable system with k degrees of freedom and action integrals $\{J_i, i = 1, \ldots, j \leq k\}$, the quantum conditions according to Sommerfeld are

$$J_i \equiv \oint p_i dq_i = n_i h, \quad i = 1, \ldots, j \tag{1.6}$$

where the n_i are non-negative integers ($j < k$ in case of degeneracy). Here it is assumed that each p_i is a periodic function of only its corresponding conjugate coordinate q_i, and the integration is taken over a period of q_i. An important principle, due to Bohr, was that slow, continuous ('adiabatic') deformations of an atomic system kept the system in a stationary state [24, 25]. Thus the action integrals for a Hamiltonian depending on parameters that vary slowly in time are conserved under slow changes of the parameters.[4] This could be applied to the problem of chemical bonding by treating the nuclear positions as the slowly varying parameters in an adiabatic transformation of the Hamiltonian for the electrons in the presence of the nuclei.

We now know that systems of more than 2 particles with Coulomb interactions may have very complicated dynamics; Newton famously struggled to account quantitatively for the orbit of the moon in the earth-moon-sun problem ($n = 3$). The underlying reason for his difficulties is the existence of solutions carrying the signature of chaos [27] and this implies that there are classical trajectories to which

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[4] This is strictly true only for integrable Hamiltonians [26].

the quantum conditions simply cannot be applied[5] because the integrals in (1.6) do not exist [28]. We also know that the r^{-1} singularity in the classical potential energy can lead to pathological dynamics in which a particle is neither confined to a bounded region, nor escapes to infinity for good. If the two-body interaction $V(\mathbf{r})$ has a Fourier transform $v(\mathbf{k})$ the total potential energy can be expressed as

$$\begin{aligned} U &= \sum_{i<j}^{n} e_i e_j V\big(|\mathbf{x}_i - \mathbf{x}_j|\big) \\ &= -\frac{n}{2} V(0) + \frac{1}{(2\pi)^3} \int d^3\mathbf{k}\, v(\mathbf{k}) \left| \sum_i e_i e^{i\mathbf{k}.\mathbf{x}_i} \right|^2 . \end{aligned}$$

In the case of the Coulomb interaction $v(\mathbf{k}) = 4\pi/k^2 > 0$ and so the potential energy U is bounded from below by $-nV(0)/2$; unfortunately for point charges as $r \to 0$, $V(r) \to \pm\infty$ and collapse may ensue [29].

Attempts were made by Born and his assistants to discuss the stationary state energy levels of 'simple' non-trivial systems such as He, H_2^+, H_2, H_2O. The molecular species were tackled as problems in *electronic structure*, that is, as requiring the calculation of the energy levels for the electron(s) in the field of *fixed* nuclei as a calculation separate from the rotation-vibration of the molecule as a whole. Pauli gave a lengthy qualitative discussion of the possible Bohr orbits for the single electron moving in the field of two fixed protons in H_2^+ but could not obtain the correct stationary states [32]. Nordheim investigated the forces between two hydrogen atoms as they approach each other adiabatically[6] in various orientations consistent with the quantum conditions. Before the atoms get close enough for the attractive and repulsive forces to balance out, a sudden discontinuous change in the electron orbits takes place and the electrons cease to revolve solely round their parent nuclei. Nordheim was unable to find an interatomic distance at which the energy of the combined system was less than that of the separated atoms; this led to the conclusion that the use of classical mechanics to discuss the stationary states of the molecular electrons had broken down comprehensively [33, 34]. This negative result was true of all the molecular calculations attempted within the Old Quantum Theory framework which was simply incapable of accounting for covalent bonding [35].

The most ambitious application of the Old Quantum Theory to molecular theory was made by Born and Heisenberg [36]. They started from the usual non-relativistic Hamiltonian (1.1) for a system comprised of n electrons and N nuclei interacting via Coulombic forces. They assumed there is an arrangement of the nuclei which is a stable equilibrium, and use that (a molecular structure) as a reference configuration

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[5] The difficulties for action-angle quantization posed by the existence of chaotic motions in non-separable systems [30] were recognized by Einstein at the time the Old Quantum Theory was developed [31].

[6] This is the earliest reference we know of where the idea of *adiabatic* separation of the electrons and the nuclei is proposed explicitly.

for the calculation. Formally the rotational motion of the system can be dealt with by requiring the coordinates for the reference structure to satisfy[7] what were later to become known as 'the Eckart conditions' [37]. Then with a suitable set of internal variables and

$$\lambda = \left(\frac{m}{M}\right)^{\frac{1}{2}}$$

as the expansion parameter, the Hamiltonian was expressed as a series

$$H = H_o + \lambda^2 H_2 + \cdots \tag{1.7}$$

to be treated by the action-angle perturbation theory Born had developed. The 'unperturbed' Hamiltonian H_o is the full Hamiltonian for the electrons with the nuclei fixed at the equilibrium structure, H_2 is quadratic in the nuclear variables (harmonic oscillators) and also contains the rotational energy,[8] while … stands for higher order anharmonic vibrational terms. H_1 may be dropped because of the equilibrium condition. With considerable effort there follows the usual separation of molecular energies, although of course no concrete calculation was possible within the Old Quantum Theory framework. It is noteworthy that their calculation gives the electronic energies at a *single* configuration because the perturbation calculation requires the introduction of the (assumed) equilibrium structure. This is different from the *adiabatic* approach Nordheim tried (unsuccessfully) to get the electronic energy at *any* separation of the nuclei [33].

1.3 Quantum Theory

With the completion of quantum mechanics in 1925–1926, the old problems in atomic and molecular theory were reconsidered and considerable success was achieved. The idea that the dynamics of the electrons and the nuclei should be treated to some extent as separate problems was generally accepted. Thus the electronic structure calculations of London [39–41] can be seen as a successful reformulation of the approach Nordheim had tried in terms of the older quantum theory, and the idea of 'adiabatic separation' is often said to originate in this work. It is however also implied in the closing section of Slater's early He atom paper where he sketches (but does not carry through) a perturbation method of approximate calculation for molecules in which the nuclei are first held fixed, and the resulting electronic eigenvalue(s) then act as the potential energy for the nuclei [42]. A quantum mechanical

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[7] This also deals with the uninteresting overall translation of the molecule.

[8] The rotational and vibrational energies occur together because of the choice of the parameter λ; as is well-known, Born and Oppenheimer later showed that a better choice is to take the quarter power of the mass ratio as this separates the vibrational and rotational energies in the orders of the perturbation expansion [38].

proof of Ehrenfest's adiabatic theorem for time-dependent perturbations was given by Born and Fock [43]. Most famously though, the quantum mechanical basis for the idea of electronic Potential Energy Surfaces is commonly attributed to Born and Oppenheimer, and it is to a consideration of their famous paper [38] that we now turn.

1.3.1 Born and Oppenheimer's Quantum Theory of Molecules

Much of the groundwork for Born and Oppenheimer's treatment of the energy levels of molecules was laid down in the earlier attempt by Born and Heisenberg [36]. The basic idea of both calculations is that the low-lying excitation spectrum of a molecule can be obtained by regarding the nuclear kinetic energy as a 'small' perturbation of the energy of the electrons for stationary nuclei *in an equilibrium configuration*. The physical basis for the idea is the large disparity between the mass of the electron and the masses of the nuclei; classically the light electrons undergo motions on a 'fast' timescale ($\tau_e \approx 10^{-16} \to 10^{-15}$ s), while the vibration-rotation dynamics of the much heavier nuclei are characterized by 'slow' timescales ($\tau_N \approx 10^{-14} \to 10^{-12}$ s).

Consider a system of electrons and nuclei and denote the properties of the former by lower-case letters (mass m, coordinates x, momenta p) and of the latter by capital letters (mass M, coordinates X, momenta P). The small parameter for the perturbation expansion must clearly be some power of m/M_o, where M_o can be taken as any one of the nuclear masses or their average. In contrast to the earlier calculation they found the correct choice is

$$\kappa = \left(\frac{m}{M_o}\right)^{\frac{1}{4}}$$

rather than Born and Heisenberg's $\lambda = \kappa^2$. In an obvious shorthand notation using a coordinate representation the kinetic energy of the electrons is then[9]

$$T_e = T_e\left(\frac{\partial}{\partial x}\right)$$

while the nuclear kinetic energy depends on κ

$$T_N = \kappa^4 H_1\left(\frac{\partial}{\partial X}\right).$$

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[9] The details can be found in the original paper [38], and in various English language presentations, for example [44–46].

The Coulomb energy is simply $U(x, X)$. They then define the 'unperturbed' Hamiltonian

$$T_e + U = H_o\left(x, \frac{\partial}{\partial x}, X\right) \tag{1.8}$$

and express the total Hamiltonian as

$$H = H_o + \kappa^4 H_1 \tag{1.9}$$

with Schrödinger equation

$$(H - E)\psi(x, X) = 0. \tag{1.10}$$

At this point in their argument they state

> Setzt man in (12) [(1.10) above] $\kappa = 0$, so bekommt man eine Differentialgleichung für die x_k allein, in der die X_l als Parameter vorkommen:
>
> $$\left\{H_o\left(x, \frac{\partial}{\partial x}; X\right) - W\right\}\psi = 0.$$
>
> Sie stellt offenbar die Bewegung der Elektronen bei festgehaltenen Kernen dar.[10]

This splitting of the Hamiltonian into an 'unperturbed' part ($\kappa = 0$) and a 'perturbation' is essentially the same as in the earlier Old Quantum Theory version [36]. The difference here is that the action-angle perturbation theory of the Old Quantum Theory is replaced by Schrödinger's quantum mechanical perturbation theory. In the following it is understood that the overall translational motion of the molecule has been separated off by a suitable coordinate transformation; this is always possible. The initial step in setting up the perturbation expansion involves rewriting the Hamiltonian H_o as a series in increasing powers of κ. This is achieved by introducing new relative coordinates that depend on κ

$$X = X_o + \kappa\zeta \tag{1.11}$$

for some fixed X_o, and using the $\{\zeta\}$ as the nuclear variables, in an expansion of H_o about X_o.

Then as usual the eigenfunction and eigenvalue of (1.10) are presented as series in κ

$$\psi = \psi^{(0)} + \kappa\psi^{(1)} + \kappa^2\psi^{(2)} + \cdots,$$
$$E = E^{(0)} + \kappa E^{(1)} + \kappa^2 E^{(2)} + \cdots,$$

the expansions are substituted into the Schrödinger equation (1.10), and the terms separated by powers of κ. This gives a set of equations to be solved sequentially.

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[10] If one sets $\kappa = 0$…one obtains a differential equation in the x_k alone, the X_l appearing as parameters:…. Evidently, this represents the electronic motion for stationary nuclei.

The crucial observation that makes the calculation successful is the choice of X_o; the Schrödinger equation for the unperturbed Hamiltonian H_o can be solved for any choice of the nuclear parameters X, and yields[11] an unperturbed energy $E(X)$ for the configuration X. For the consistency of the whole scheme however it turns out (cf. footnote 9) that X_o in (1.11) cannot be arbitrarily chosen, but must correspond to a *minimum* of the electronic energy. That there is such a point is assumed to be self-evident for the case of a stable molecule. The result of the calculation was a triumph; the low-lying energy levels of a stable molecule can be written in the form

$$E_{\text{Mol}} = E_{\text{Elec}} + \kappa^2 E_{\text{Vib}} + \kappa^4 E_{\text{Rot}} + \cdots \tag{1.12}$$

in agreement with a considerable body of spectroscopic evidence. The eigenfunctions that correspond to these energy levels are simple products of an electronic wavefunction obtained for the equilibrium geometry and suitable vibration-rotation wavefunctions for the nuclei.

The Born and Heisenberg calculation [36] had been performed while Heisenberg was a student with Born; Kragh [35] quotes Heisenberg's later view of it in the following terms

> As an exasperated Heisenberg wrote to Pauli, "The work on molecules I did with Born… contains bracket symbols [Klammersymbole] with up to 8 indices and will probably be read by no one." Certainly, it was not read by the chemists.

Curiously that may have initially been the fate of Born and Oppenheimer's paper. As noted by one of us many years ago, a survey of the literature up to about 1935 shows that the paper was hardly if ever mentioned, and when it was mentioned, its arguments were used as *a posteriori* justification for what was being done anyway [47]. What was being done was the general use in molecular spectroscopy and chemical reaction theory of the idea of Potential Energy Surfaces on which the nuclei moved. As we have seen, that idea is *not* to be found in the approach taken by Born and Oppenheimer which used (and had to use) a single privileged *point* in the nuclear configuration space—the assumed equilibrium arrangement of the nuclei [38].

In 1935 a significant event was the publication of the famous textbook *Introduction to Quantum Mechanics* [48] which was probably the first textbook concerned with quantum mechanics that addressed in detail problems of interest to chemists. Generations of chemists and physicists took their first steps in quantum theory with this book, which is still available in reprint form. Chapter X of the book is entitled *The Rotation and Vibration of Molecules*; it starts by summarizing the empirical results of molecular spectroscopy which are consistent with (1.12). The authors then turn to the wave equation for a general collection of electrons and nuclei and remark that its Schrödinger wave equation may be solved approximately by a procedure that they attribute to Born and Oppenheimer; first solve the wave equation for the electrons alone, with the nuclei in a fixed configuration, and then solve the wave equation for the nuclei alone, in which a characteristic energy value [eigenvalue] of

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[11] $W(X)$ in the notation of the above quotation.

the electronic wave equation, regarded as a function of the internuclear distances, occurs as a potential function. After some remarks about the coordinates they say

> The first step in the treatment of a molecule is to solve this electronic wave equation for all configurations of the nuclei. It is found that the characteristic values $U_n(\xi)$ of the electronic energy are continuous functions of the nuclear coordinates ξ. For example, for a free diatomic molecule the electronic energy function for the most stable electronic state ($n = 0$) is a function only of the distance r between the two nuclei, and it is a continuous function of r, such as shown in Fig. 34-2.

Figure 34-2 referred to here is a Morse potential function. Later in the book where they give a brief introduction to activation energies of chemical reactions they explicitly cite London [41] as the origin of the idea of adiabatic nuclear motion on a Potential Energy Surface, though there is also a nod back towards Chap. X. Although it is now almost universal practice to refer to treating the nuclei as classical particles that give rise to an electronic energy surface as 'making the Born-Oppenheimer approximation' it is our opinion that the justification for such a strategy is not to be found in *The Quantum Theory of Molecules*, [38]. Nor is it to be found in the early papers of London [39–41] where it was simply assumed as a reasonable thing to do. And it is certainly the case that Born and Oppenheimer did *not* show the electronic energy to be a continuous function of the nuclear coordinates; that was first demonstrated for a diatomic molecule forty years after Pauling and Wilson's book was published (see Sect. 1.3.4).

1.3.2 Born and the Elimination of Electronic Motion

Many years after his work with Heisenberg and Oppenheimer, Born returned to the subject of molecular quantum theory and developed a different account of the separation of electronic and nuclear motion [44, 49]. It is to this method that the expression 'Born-Oppenheimer approximation' usually refers in modern work. Consider the unperturbed electronic Hamiltonian $H_o(x, X_f)$ at a fixed nuclear configuration X_f that corresponds to some molecular structure (not necessarily an equilibrium structure). The Schrödinger equation for H_o is

$$\big(H_o(x, X_f) - E^o(X_f)_m\big)\varphi(x, X_f)_m = 0. \tag{1.13}$$

This equation can have both bound-state and continuum eigenfunctions; the *bound-state* eigenvalues considered as functions of the X_f are the molecular Potential Energy Surfaces. Born proposed to solve the full molecular Schrödinger equation, (1.10) by an expansion

$$\psi(x, X) = \sum_m \Phi(X)_m \varphi(x, X)_m \tag{1.14}$$

with coefficients $\{\Phi(X)_m\}$ that play the role of nuclear wavefunctions. As in the original calculation (Sect. 1.3.1) a crucial step is to assign the nuclear coordinates the role of parameters in the Schrödinger equation (1.13) for the electronic Hamiltonian; it differs from the earlier approach of Born and Oppenheimer because now the values of X_f range over the whole nuclear configuration space. Substituting this expansion into (1.10), multiplying the result by $\varphi(x, X)_n^*$ and integrating over the electronic coordinates x leads to an infinite dimensional system of coupled equations for the nuclear functions $\{\Phi\}$,

$$\big(T_N + E^o(X)_n - E\big)\Phi(X)_n + \sum_{nn'} C(X, P)_{nn'}\Phi(X)_{n'} = 0 \tag{1.15}$$

where the coupling coefficients $\{C(X, P)_{nn'}\}$ have a well-known form which we need not record here [44].

In this formulation the adiabatic approximation consists of retaining only the diagonal terms in the coupling matrix $\mathbf{C}(X, P)$, for then a state function can be written as

$$\psi(x, X) \approx \psi(x, X)_n^{\mathrm{AD}} = \varphi(x, X)_n\Phi(X)_n \tag{1.16}$$

and a product wavefunction corresponds to additive electronic and nuclear energies. The special character of the electronic wavefunctions $\{\varphi(x, X)_m\}$ is, by (1.13), that they diagonalize the electronic Hamiltonian H_o; they are said to define an 'adiabatic' basis (cf. the approximate form (1.16)) because the electronic state label n is not altered as X varies. The Born approach does not really require the diagonalization of H_o; it is perfectly possible to define other representations of the electronic expansion functions through unitary transformations of the $\{\varphi\}$, with concomitant modification of the coupling matrix $\mathbf{C}$. This leads to so-called 'diabatic' bases; the freedom to choose the representation is very important in practical applications to spectroscopy and atomic/molecular collisions [50, 51].

1.3.3 Formal Quantum Theory of the Molecular Hamiltonian

We now start again and develop the quantum theory of the Hamiltonian for a collection of n charged particles with Coulombic interactions.[12] We remind ourselves again from Sect. 1.1 that for particles with classical Hamiltonian variables $\{\mathbf{q}_i, \mathbf{p}_i\}$ this is

$$\mathsf{H} = \sum_i^n \frac{p_i^2}{2m_i} + \sum_{i<j}^n \frac{e_i e_j}{4\pi\varepsilon_0|\mathbf{q}_i - \mathbf{q}_j|} \tag{1.17}$$

with the non-zero Poisson-bracket

$$\{\mathbf{x}_i, \mathbf{p}_j\} = \delta_{ij}.$$

---

[12] The reader may find it helpful to refer to the Appendix which summarizes some mathematical notions that are needed here, and illustrates them in a simple model of coupled oscillators with two degrees of freedom.

Let us denote the classical dynamical variables for the electrons collectively as $\mathbf{x}, \mathbf{p}$, and those for the nuclei by $\mathbf{X}, \mathbf{P}$ and denote the classical Hamiltonian by $\mathsf{H}(\mathbf{x}, \mathbf{p}, \mathbf{X}, \mathbf{P})$. After the customary canonical quantization these variables become time-independent operators in a Schrödinger representation

$$\mathbf{x} \rightarrow \hat{\mathbf{x}} \quad etc.$$

In the following it will be important to distinguish between operators and c-numbers, so in the following we will use the $\hat{\mathbf{x}}$ notation for operators, and make no special choice of representation.

As we have seen, the idea that the kinetic energy of the massive nuclei could be treated as a perturbation of the electronic motion was first formulated in the framework of the Old Quantum Theory. The idea was to separate the classical Hamiltonian H into two parts to isolate the nuclear momentum variables

$$\mathsf{H}(\mathbf{x}, \mathbf{p}, \mathbf{X}, \mathbf{P}) = H_o(\mathbf{x}, \mathbf{p}, \mathbf{X}) + \kappa^4 H_1(\mathbf{P}). \tag{1.18}$$

According to Hamilton's equations for the unperturbed problem

$$\frac{d\mathbf{X}}{dt} = \{\mathbf{X}, H_o\} = 0, \tag{1.19}$$

using Poisson-bracket notation, which was interpreted (correctly) as describing the dynamics of the electrons in the field of stationary nuclei. This was the starting point of Born and Heisenberg's calculations [36].

Let us now move to quantum theory and recast (1.18) as an operator relation, writing the molecular Hamiltonian operator as

$$\hat{\mathsf{H}}(\hat{\mathbf{x}}, \hat{\mathbf{p}}, \hat{\mathbf{X}}, \hat{\mathbf{P}}) = \hat{H}_o(\hat{\mathbf{x}}, \hat{\mathbf{p}}, \hat{\mathbf{X}}) + \kappa^4 \hat{H}_1(\hat{\mathbf{P}}) \tag{1.20}$$

with equation of motion under $\hat{H}_o$

$$i\hbar \frac{d\hat{\mathbf{X}}}{dt} = [\hat{\mathbf{X}}, \hat{H}_o] = 0 \tag{1.21}$$

from which we infer the nuclear position operators $\hat{\mathbf{X}}$ are constants of the motion under $\hat{H}_o$. We no longer make the interpretation that follows from (1.19) since specifying precisely the positions $\{\mathbf{X}\}$ for *stationary* nuclei violates the Uncertainty Principle. Instead (1.21) leads to a completely different conclusion (see below).

We must now take a little bit of care about the definition of the variables, and dispose of the uninteresting overall motion of the molecule [4]. Since the Coulomb interaction only depends on interparticle distances it is translation invariant, and therefore the total momentum operator $\hat{\mathsf{P}}$

$$\hat{\mathsf{P}} = \sum_n \hat{\mathbf{p}}_n$$

commutes with $\hat{\mathsf{H}}$. It follows that the molecular Hamiltonian may be written as a direct integral

$$\hat{\mathsf{H}} = \int_{\mathbf{R}^3}^{\oplus} \hat{H}(P)dP \tag{1.22}$$

where [52]

$$\hat{H}(P) = \frac{P^2}{2M_T} + \hat{\mathsf{H}}' \tag{1.23}$$

is the Hamiltonian at fixed total momentum P and M_T is the molecular mass. The internal Hamiltonian $\hat{\mathsf{H}}'$ is independent of the centre-of-mass variables and is explicitly translation invariant. The form of $\hat{\mathsf{H}}'$ is not uniquely fixed but whatever coordinates are chosen the essential point is that it is always the same operator specified in (1.23) acting on a Hilbert space $\mathfrak{H}$ that may be parameterized by functions of the electron and nuclear coordinates.

The separation of the centre-of-mass terms from the internal Hamiltonian is the same in quantum mechanics as in classical mechanics so we need not distinguish operators from classical variables in this step. It is convenient to choose the centre-of-nuclear mass for the definition of suitable internal coordinates.[13] Let $\mathbf{t}^{\mathrm{e}}$ be a set of internal electronic coordinates defined as the original electronic coordinates $\mathbf{x}$ referred to the centre-of-nuclear mass, and let $\mathbf{t}^{\mathrm{n}}$ be a set of internal nuclear coordinates constructed purely from the original nuclear coordinates $\mathbf{X}$. If there are s electrons and M nuclei, there are s internal electronic coordinates, and $M - 1$ internal nuclear coordinates. There are corresponding canonically conjugate internal momentum variables. In terms of these variables the total kinetic energy of all the particles can be decomposed into the form

$$\mathsf{T}_0 = \mathsf{T}_{\mathrm{CM}} + \mathsf{T}_{\mathrm{N}} + \mathsf{T}_{\mathrm{e}} \tag{1.24}$$

where T_{CM} is the kinetic energy for the centre-of-mass, T_{N} is the kinetic energy for the nuclei expressed purely in terms of the internal nuclear momentum variables, and T_{e} is the kinetic energy for the electrons expressed purely in terms of the internal electronic momentum variables. The Coulomb energy can be expressed purely in terms of the internal coordinates, $U = U(\mathbf{t}^{\mathrm{e}}, \mathbf{t}^{\mathrm{n}})$. These relations are true both classically and in quantum mechanics with a suitable operator interpretation.

In parallel with the decomposition in (1.18), we define the quantum mechanical 'electronic' Hamiltonian as

$$\hat{\mathsf{H}}^{\mathrm{elec}} = \hat{\mathsf{T}}_{\mathrm{e}} + \hat{U}\left(\hat{\mathbf{t}}^{\mathrm{e}}, \hat{\mathbf{t}}^{\mathrm{n}}\right) \tag{1.25}$$

---

[13] It is always possible to split off the kinetic energy of the centre-of-mass without any approximation; with this choice we retain the separation of the electronic and nuclear kinetic energies as well, as in (1.24). Explicit formulae are given in e.g. [3] where it is shown that the nuclear kinetic energy terms involve reciprocals of the nuclear masses, so that overall, the nuclear kinetic energy is proportional to κ^4.

so that after dropping the uninteresting kinetic energy for the overall centre-of-mass, we see that the internal Hamiltonian has the form,

$$\hat{\mathsf{H}}' = \hat{\mathsf{H}}^{\text{elec}} + \hat{\mathsf{T}}_{\text{N}} \tag{1.26}$$

where, as before, the nuclear kinetic energy term is proportional to κ^4 (see footnote 13). Its Schrödinger equation may be written

$$\hat{\mathsf{H}}'|\Psi_m\rangle = E_m|\Psi_m\rangle \tag{1.27}$$

where m is used to denote a set of quantum numbers $(J\ M\ p\ r\ i)$: J and M for the angular momentum state: p specifying the parity of the state: r specifying the permutationally allowed irreducible representations within the groups of identical particles, and i to specify a particular energy value. Any bound state (a 'molecule') has an energy lying below the start of the essential spectrum.

Now just as in (1.21) $\hat{\mathsf{H}}^{\text{elec}}$ is independent of the nuclear momentum operators and so it commutes with the internal nuclear position operators

$$\left[\hat{\mathsf{H}}^{\text{elec}}, \hat{t}^{\text{n}}\right] = 0. \tag{1.28}$$

They may therefore be simultaneously diagonalized and we use this property to characterize the Hilbert space $\mathscr{H}$ for $\hat{\mathsf{H}}^{\text{elec}}$. Let $\mathbf{b}$ be some eigenvalue of the $\hat{\mathbf{t}}^{\text{n}}$ corresponding to choices $\{\mathbf{x}_g = \mathbf{a}_g, g = 1, \ldots, M\}$ in the laboratory-fixed frame; then the $\{\mathbf{a}_g\}$ describe a classical nuclear geometry. The set, X, of all $\mathbf{b}$ is $\mathbf{R}^{3(M-1)}$. We denote the Hamiltonian $\hat{\mathsf{H}}^{\text{elec}}$ evaluated at the nuclear position eigenvalue $\mathbf{b}$ as $\hat{\mathsf{K}}(\mathbf{b}, \hat{\mathbf{t}}^{\text{e}})_o = \hat{\mathsf{K}}_o$ for short; this $\hat{\mathsf{K}}_o$ is very like the usual clamped-nuclei Hamiltonian but it is explicitly translationally invariant, and has an extra term, which is often called the Hughes-Eckart term, or the mass polarization term. Its Schrödinger equation is of the same form as (1.13), with eigenvalues $E^o(\mathbf{b})_k$ and corresponding eigenfunctions $\varphi(\mathbf{t}^{\text{e}}, \mathbf{b})_k$,

$$\hat{\mathsf{K}}_o\varphi\big(\mathbf{b}, \mathbf{t}^{\text{e}}\big)_k = E^o(\mathbf{b})_k\varphi\big(\mathbf{b}, \mathbf{t}^{\text{e}}\big)_k. \tag{1.29}$$

As before its spectrum in general contains a discrete part below a continuum,

$$\sigma(\mathbf{b}) \equiv \sigma\big(\hat{\mathsf{K}}\big(\mathbf{b}, \hat{\mathbf{t}}^{\text{e}}\big)_o\big) = \big[E^o(\mathbf{b})_0, \ldots, E^o(\mathbf{b})_m\big) \bigcup \big[\Lambda(\mathbf{b}), \infty\big). \tag{1.30}$$

Note that for other than diatomic molecules, it is not possible to proceed further and separate out explicitly the rotational motion. For any choice of $\mathbf{b}$ the eigenvalues of $\hat{\mathsf{K}}_o$ will depend only upon the shape of the geometrical figure formed by the $\{\mathbf{a}_g\}$, being independent of its orientation. It is possible to introduce a so-called body-fixed frame by transforming to a new coordinate system built out of the $\mathbf{b}$ consisting of three angular variables and $3M - 6$ internal coordinates. In so doing however one cannot avoid angular momentum terms arising which couple the electronic and nuclear variables, and so there is no longer a clean separation of the kinetic energy into an electronic and a nuclear part. Moreover no *single* specification of body-fixed coordinates can be given that describes *all* possible nuclear configurations.

The internal molecular Hamiltonian $\hat{\mathsf{H}}'$ in (1.23) and the clamped-nuclei like operator $\hat{\mathsf{K}}_o$ just defined can be shown to be essentially self-adjoint (on their respective Hilbert spaces) by reference to the Kato-Rellich theorem [53] because in both cases there are kinetic energy operators that dominate the (singular) Coulomb interaction; they therefore have a complete set of eigenfunctions. As regards $\hat{\mathsf{H}}^{\text{elec}}$, we have a family of Hilbert spaces $\{\mathscr{H}(\mathbf{b})\}$ which are parameterized by the nuclear position vectors $\mathbf{b} \in X$ that are the 'eigenspaces' of the family of self-adjoint operators $\hat{\mathsf{K}}_o$; from them we can construct a big Hilbert space as a direct integral over all the $\mathbf{b}$ values

$$\mathscr{H} = \int_X^{\oplus} \mathscr{H}(\mathbf{b}) d\mathbf{b} \tag{1.31}$$

and this is the Hilbert space for $\hat{\mathsf{H}}^{\text{elec}}$ in (1.25).

Equation (1.31) leads directly to a fundamental result; since $\hat{\mathsf{H}}^{\text{elec}}$ commutes with all the $\{\hat{t}^{\text{n}}\}$, it has the direct integral decomposition

$$\hat{\mathsf{H}}^{\text{elec}} = \int_X^{\oplus} \hat{\mathsf{K}}\big(\mathbf{b}, \hat{\mathbf{t}}^{\text{e}}\big)_o d\mathbf{b}. \tag{1.32}$$

Even if the ' clamped-nuclei' Hamiltonian has a set of discrete states—Potential Energy Surfaces—(1.32) implies that the unperturbed Hamiltonian,[14] $\hat{\mathsf{H}}^{\text{elec}}$, *has purely continuous spectrum* (cf. Appendix),

$$\sigma = \sigma\big(\hat{\mathsf{H}}^{\text{elec}}\big) = \bigcup_{\mathbf{b}} \sigma(\mathbf{b}) \equiv [V_0, \infty)$$

where V_0 is the minimum value of $E(\mathbf{b})_0$; in the diatomic molecule case this is the minimum value of the usual ground-state potential energy curve $E_0(r)$. The operator $\hat{\mathsf{H}}^{\text{elec}}$ has no localized eigenfunctions; rather, its eigenfunctions are continuum functions. To avoid any misunderstanding, we emphasize that this result has nothing to do with the continuous spectrum of the full molecular Hamiltonian associated with the centre-of-mass motion which can be dealt with trivially in the preliminaries.

A possibly helpful way to think about this paradoxical result is as follows. The quantum mechanical molecular Hamiltonian for a collection of electrons and nuclei with Coulomb interactions is a function of position and momentum operators for all the specified electrons and all the nuclei. If now we separate off the terms containing all the nuclear momentum operators (the terms proportional to κ^4) what is left must be a function of position and momentum operators for the electrons *and position operators for all the nuclei*. This statement is true in any representation of the operators, and in particular must be respected if one chooses a position representation.

This is *not* what Born and Oppenheimer assumed about their equation (12) [our equation (1.10)] when $\kappa = 0$—see Sect. 1.3.1 above—and which has been assumed ever since in Quantum Chemistry. In effect they chose to work only in the 'small'

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[14] After the elimination of the centre-of-mass variables $\hat{\mathsf{H}}^{\text{elec}}$ is playing the role of $\hat{H}_o$ in (1.20).

Hilbert space of a fixed configuration, $\mathscr{H}(\mathbf{X})$, in which $\mathbf{X}$ can be assumed to be a 'parameter' in the position space wavefunction $\psi(\mathbf{x}, \mathbf{X})$, whereas if they had continued with quantum mechanics they would have been working in the 'big' Hilbert space $\mathscr{H}$ with $\hat{\mathbf{x}}$ and $\hat{\mathbf{X}}$ treated on an equal footing as operators, and all possible nuclear configurations being treated simultaneously, rather than one at a time.

The unusual properties of the ('electronic') Hamiltonian $\hat{\mathsf{H}}_o(\hat{\mathbf{x}}, \hat{\mathbf{p}}, \hat{\mathbf{X}}) = \hat{\mathsf{H}}^{\text{elec}}$ in (1.32)[15] considered as a quantum-mechanical operator on the whole space $\mathfrak{H}$, are of exactly the kind to be expected from the work of Kato [54]. In Lemma 4 of his paper he showed that for a Coulomb potential U and for any function f in the domain $\mathcal{D}_0$ of the full kinetic energy operator $\hat{\mathsf{T}}_0$, the domain, $\mathcal{D}_U$, of the internal Hamiltonian $\hat{\mathsf{H}}'$ contains $\mathcal{D}_0$ and there are two constants a, b such that

$$\|Uf\| \leq a\|\hat{\mathsf{T}}_0 f\| + b\|f\|$$

where a can be taken as small as is liked. This result is often summarised by saying that the Coulomb potential is small compared to the kinetic energy. Given this result he proved in Lemma 5 (the Kato-Rellich theorem) that the usual Coulomb Hamiltonian operator is essentially self-adjoint and so is guaranteed a complete set of eigenfunctions, and is bounded from below.

In the present context the important point to note is that the Coulomb term is small only in comparison with the kinetic energy term involving the same set of variables. So the absence of one or more kinetic energy terms from the Hamiltonian may mean that the Coulomb potential term cannot be treated as small. It is evident that one can't use the Kato-Rellich argument to guarantee self-adjointness for the customary representation of H^{elec} in a position representation as a differential and multiplicative operator because it contains the nuclear positions $\{\mathbf{X}\}$ in Coulomb terms that are not dominated by corresponding kinetic energy operators involving the conjugate momentum operators $\{-i\hbar\nabla\}$ since they have been separated off into the 'perturbation' term $\propto \kappa^4$. As a quite separate matter, the abstract direct integral operator (1.32) is self-adjoint since the resolvent of the clamped-nuclei Hamiltonian is integrable. This is demonstrated in Theorem XIII.85 in the book by Reed and Simon [53]. It is in this form that the operator is used in the mathematically rigorous accounts (to be discussed later) of the Born-Oppenheimer approximation in [64] and [70]. The operator used in the standard account of Born and Huang [44] is however simply the usual one which, as discussed above, is not self-adjoint in the Kato sense.

1.3.4 Approximate Calculations

It might have been hoped, in the light of the claim in the original paper by Born and Oppenheimer quoted in Sect. 1.3.1, that the eigensolutions of the $\kappa \to 0$ limit

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[15] We assume that the centre-of-mass contributions are eliminated as usual.

of the internal Hamiltonian, $\hat{\mathsf{H}}'$, would actually be those that would have been obtained from (1.10) after separation of the centre-of-mass term, by letting the nuclear masses increase without limit. Although there are no analytically solved molecular problems, the work of Frolov [55] provides extremely accurate numerical solutions for a problem with two nuclei and a single electron. Frolov investigated what happens when the masses of one and then two of the nuclei increase without limit in his calculations. To appreciate his results, consider a system with two nuclei; the natural nuclear coordinate is the internuclear distance which will be denoted here simply as $\mathbf{t}$. When needed to express the electron-nuclei attraction terms, $\mathbf{x}_i^{\mathrm{n}}$ is simply of the form $\alpha_i \mathbf{t}$ where α_i is a signed ratio of the nuclear mass to the total nuclear mass; in the case of a homonuclear system $\alpha_i = \pm\frac{1}{2}$.

The di-nuclear electronic Hamiltonian after the elimination of the centre-of-mass contribution as described in Sect. 1.3.3 is

$$\begin{aligned}\hat{\mathsf{H}}^{\mathrm{elec}}(\mathbf{t}^{\mathrm{e}}, \mathbf{t}) = &-\frac{\hbar^2}{2m}\sum_{i=1}^{N} \nabla^2(\mathbf{t}_i^{\mathrm{e}}) - \frac{\hbar^2}{2(m_1+m_2)} \sum_{i,j=1}^{N} \nabla(\mathbf{t}_i^{\mathrm{e}}) \cdot \nabla(\mathbf{t}_j^{\mathrm{e}}) \\ &- \frac{e^2}{4\pi\varepsilon_0}\sum_{j=1}^{N}\left(\frac{Z_1}{|\mathbf{t}_j^{\mathrm{e}} + \alpha_1\mathbf{t}|} + \frac{Z_2}{|\mathbf{t}_j^{\mathrm{e}} + \alpha_2\mathbf{t}|}\right) \\ &+ \frac{e^2}{8\pi\varepsilon_0}\sum_{i,j=1}^{N}{}' \frac{1}{|\mathbf{t}_i^{\mathrm{e}} - \mathbf{t}_j^{\mathrm{e}}|} + \frac{Z_1 Z_2}{R}, \qquad R = |\mathbf{t}| \end{aligned} \tag{1.33}$$

while the nuclear kinetic energy part is:

$$\hat{\mathsf{T}}_{\mathrm{N}}(\mathbf{t}) = -\frac{\hbar^2}{2}\left(\frac{1}{m_1} + \frac{1}{m_2}\right)\nabla^2(\mathbf{t}) \equiv -\frac{\hbar^2}{2\mu}\nabla^2(\mathbf{t}). \tag{1.34}$$

The full internal motion Hamiltonian for the three-particle system is then

$$\hat{\mathsf{H}}'(\mathbf{t}^{\mathrm{e}}, \mathbf{t}) = \hat{\mathsf{H}}^{\mathrm{elec}}(\mathbf{t}^{\mathrm{e}}, \mathbf{t}) + \hat{\mathsf{T}}_{\mathrm{N}}(\mathbf{t}) \tag{1.35}$$

which is of the same form as (1.26).

It is seen from (1.34), that if only one nuclear mass increases without limit then the kinetic energy term in the nuclear variable remains in the full problem and so the Hamiltonian (1.35) remains essentially self-adjoint. Frolov's calculations showed that when one mass increased without limit (the atomic case), any discrete spectrum persisted but when two masses were allowed to increase without limit (the molecular case), the Hamiltonian ceased to be well-defined and this failure led to what he called *adiabatic divergence* in attempts to compute discrete eigenstates of (1.35). This divergence is discussed in some mathematical detail in the Appendix to Frolov [55]. It does not arise from the choice of a translationally invariant form for the electronic Hamiltonian; rather it is due to the lack of any kinetic energy term to dominate the Coulomb potential.

To every solution of (1.29) there corresponds a function

$$\Phi\left(\mathbf{t}^{\mathrm{e}},\mathbf{t}^{\mathrm{n}}\right)_m = \varphi\left(\mathbf{b},\mathbf{t}^{\mathrm{e}}\right)_m \delta\left(\mathbf{t}^{\mathrm{n}}-\mathbf{b}\right) \tag{1.36}$$

in the $(\mathbf{t}^{\mathrm{e}},\mathbf{t}^{\mathrm{n}})$ position representation which is a formal solution, in the sense of distributions, of the Schrödinger equation for $\hat{\mathsf{H}}^{\mathrm{elec}}$. The energy, $\mathscr{E}_m(\mathbf{b})$ of the function (1.36) is independent of the orientation of the figure defined by the $\mathbf{b}$, and is also unaltered by the parity operation $\mathbf{b} \to -\mathbf{b}$, and by permutations of the labelling of any identical nuclei. Φ_m however depends on the orientation of the body-fixed frame defined by the configuration $\mathbf{b}$ with respect to some space-fixed reference frame. Let the Euler angles relating these two frames be Ω so that

$$\Phi(\mathbf{b})_m = \Phi(\overline{\mathbf{b}},\Omega)_m$$

in an obvious notation, so we have a continuous family of degenerate states. The dependence on orientation is eliminated by forming a continuous superposition through integration over the Euler angles with some weight function $c(\Omega)$

$$\Psi_m = \int d\Omega' c\left(\Omega'\right)\Phi\left(\overline{\mathbf{b}},\Omega'\right)_m.$$

Similarly one may form superpositions of the space-inverted and permuted states in order to form a new basis that displays the corresponding symmetries that leave the energy eigenvalue unchanged.

There are two quite distinct approaches to the solution of the molecular Schrödinger equation (1.27) based on the formal theory reviewed in Sect. 1.3.3. Functions of the type (1.36) can be used as the basis of a Rayleigh-Ritz calculation being, hopefully, well-adapted to the construction of useful trial functions. Several different lines have been developed; in the *adiabatic* model the trial function is written as the continuous linear superposition

$$\begin{aligned}\Psi\left(\mathbf{t}^{\mathrm{e}},\mathbf{t}^{\mathrm{n}}\right)_m &= \int d\mathbf{b}F(\mathbf{b})\varphi\left(\mathbf{b},\mathbf{t}^{\mathrm{e}}\right)_m\delta\left(\mathbf{t}^{\mathrm{n}}-\mathbf{b}\right)\\ &= F\left(\mathbf{t}^{\mathrm{n}}\right)\varphi\left(\mathbf{t}^{\mathrm{n}},\mathbf{t}^{\mathrm{e}}\right)_m\end{aligned} \tag{1.37}$$

where the square-integrable weight factor $F(\mathbf{t}^{\mathrm{n}})$ may be determined by reducing (1.27) to an effective Schrödinger equation for the nuclei in which $F(\mathbf{t}^{\mathrm{n}})$ appears as the eigenfunction [56].

If the $\{\varphi_m\}$ are chosen to be orthonormal we have

$$\langle\Psi_m|\Psi_m\rangle = \iint d\mathbf{t}^{\mathrm{e}}d\mathbf{t}^{\mathrm{n}}\left|\Psi\left(\mathbf{t}^{\mathrm{e}},\mathbf{t}^{\mathrm{n}}\right)_m\right|^2 = \int d\mathbf{t}^{\mathrm{n}}\left|F\left(\mathbf{t}^{\mathrm{n}}\right)\right|^2.$$

We may choose the weight factor F to be normalized, so that the state function Ψ_m is also normalized. On the other hand

$$\langle\Psi_m|\hat{\mathsf{H}}'|\Psi_m\rangle = \iint d\mathbf{t}^{\mathrm{e}}d\mathbf{t}^{\mathrm{n}}\Psi_m^*\left(\hat{\mathsf{H}}'\Psi_m\right) = \int d\mathbf{t}^{\mathrm{n}}F\left(\mathbf{t}^{\mathrm{n}}\right)^*(\hat{\mathsf{H}}_m F)\left(\mathbf{t}^{\mathrm{n}}\right)$$

where we have defined the effective nuclear Hamiltonian

$$(\hat{\mathsf{H}}_m F)(\mathbf{t}^{\mathrm{n}}) = \int d\mathbf{t}^{\mathrm{e}} \varphi(\mathbf{t}^{\mathrm{e}}, \mathbf{t}^{\mathrm{n}})_m \left[\hat{\mathsf{H}}' \varphi(\mathbf{t}^{\mathrm{e}}, \mathbf{t}^{\mathrm{n}})_m F(\mathbf{t}^{\mathrm{n}})\right]. \tag{1.38}$$

The Rayleigh-Ritz quotient

$$E[\Psi_m] = \frac{\langle \Psi_m | \hat{\mathsf{H}}' | \Psi_m \rangle}{\langle \Psi_m | \Psi_m \rangle} \tag{1.39}$$

is stationary for those functions that are solutions of the effective nuclear 'Schrödinger equation'

$$\hat{\mathsf{H}}_m F_s = E_{ms} F_s. \tag{1.40}$$

In particular, using the electronic ground state φ_0, the Rayleigh-Ritz quotient leads to an *upper bound* to the ground state energy E_0 of $\hat{\mathsf{H}}'$. Having set up the calculation with square integrable functions the approximate ground-state is naturally a discrete state; the discussion however yields no information about the bottom of the essential spectrum i.e. it does not prove the existence of a bound-state below the continuum. This calculation amounts to the diagonalization of the projection of $\hat{\mathsf{H}}'$ on the one-dimensional subspace spanned by Ψ_0. In principle the subspace may be enlarged, and the accuracy thereby improved, by using the subspace spanned by a set of trial functions $(\Psi_0, \Psi_1, \ldots, \Psi_m)$ of the form of (1.37). Such non-adiabatic calculations which make no use of a Potential Energy Surface are restricted to very small molecules.

In practice the variational approach is implemented as follows; a collection of energies $E(\mathbf{b}_i)$ is found through standard quantum chemical computations for different geometries $\{\mathbf{b}_i\}$ and fitted to produce a function $V(\mathbf{t}^{\mathrm{n}})$ that is treated as a potential energy contribution to the left-hand-side of the Born equation (1.15), rather than (1.40), so the clamped-nuclei assumption enters in an essential way (see Appendix). With considerable computational effort it is possible to construct permutationally invariant energy surfaces for molecules with up to 10 nuclei [57]. Note however that if $\hat{\mathsf{H}}'$ is separated as in (1.26), then it is $\hat{\mathsf{H}}^{\mathrm{elec}}$ that appears in (1.38) rather than the clamped-nuclei Hamiltonian.

Another generalization is to replace the unnormalizable delta function in (1.37) by a square integrable function; the relation

$$\delta^3(\mathbf{x} - \mathbf{y}) = \lim_{a \to \infty} \left(\frac{a}{\pi}\right)^{\frac{3}{2}} e^{-a(\mathbf{x}-\mathbf{y})^2} \equiv \lim_{a \to \infty} \chi_a(\mathbf{x}, \mathbf{y})$$

suggests that one might consider trial wavefunctions

$$\Psi(\mathbf{t}^{\mathrm{e}}, \mathbf{t}^{\mathrm{n}})_m^{\mathrm{GCM}} = \int d\mathbf{b} F(\mathbf{b}) \varphi(\mathbf{b}, \mathbf{t}^{\mathrm{e}})_m \chi_a(\mathbf{t}^{\mathrm{n}}, \mathbf{b})$$

for some suitably chosen parameter a. This is the basis of the molecular *Generator Coordinate Method* (GCM) which is a non-adiabatic formalism; as before the weight factor $F(\mathbf{b})$ is determined by appeal to the Rayleigh-Ritz quotient, although part of its structure can be determined purely by symmetry arguments. In the GCM the effective Schrödinger equation for the weight function becomes an integral equation (the Hill-Wheeler equation) [45]. Again the trial function may be improved, in the sense of a variational calculation, by forming linear superpositions of the wavefunctions $\{\Psi^{\mathrm{GCM}}\}$; this has been done for diatomic molecules for which a fairly complete GCM account has been developed [45, 58]. Usually however the dependence on the nuclear variables $\{\mathbf{t}^{\mathrm{n}}\}$ is not expressed through functions adapted to nuclear permutation symmetry, and the GCM weight functions are determined by molecular structure considerations.

It should be noted here that $\varphi(\mathbf{b}, \mathbf{t}^{\mathrm{e}})$ as a solution to the Schrödinger equation (1.29) where $\mathbf{t}^{\mathrm{n}}$ has been replaced by $\mathbf{b}$, is defined only up to a phase factor of the form

$$\exp\left[iw(\mathbf{b})\right]$$

w is any single-valued real function of the $\{\mathbf{b}_i\}$ which can be different for different electronic states. The phase factor is only trivial in the absence of degeneracies. Specific phase choices may therefore be needed when tying this part to the nuclear part of the product wave function. It is only by making suitable phase choices that the electronic wave function is made a continuous function of the formal nuclear variables, $\mathbf{b}$, and the complete product function, made single valued. This is the origin of the Berry phase in clamped-nuclei calculations involving intersecting Potential Energy Surfaces; for a discussion of these matters see [59, 60]. It is worth noting explicitly that notions of molecular Berry phases and conical intersections of PE surfaces are tied to the clamped-nuclei viewpoint which introduces 'adiabatic parameters'. According to quantum mechanics the eigensolutions of (1.27) are single-valued functions by construction with arbitrary phases (rays) so one does not expect any Berry phase phenomena *a priori*.

The rigorous mathematical analysis of the original perturbation approach proposed by Born and Oppenheimer [38] for a molecular Hamiltonian with Coulombic interactions was initiated by Combes and co-workers [61–64] with results for the diatomic molecule. Some properties of the operator $\mathsf{H}^{\mathrm{elec}}$, (1.32), seem to have been first discussed in this work. A perturbation expansion in powers of κ leads to a singular perturbation problem because κ is a coefficient of differential operators of the highest order in the problem; the resulting series expansion of the energy is an *asymptotic* series, closely related to the WKB approximation obtained by a semiclassical analysis of the effective Hamiltonian for the nuclear dynamics. This requires a more complete treatment than the adiabatic model using the partitioning technique to project the full Coulomb Hamiltonian, $\hat{\mathsf{H}}'$, onto the adiabatic subspace. A normalized electronic eigenvector $|\varphi(\mathbf{b})_j\rangle$ is associated with a projection operator by the usual correspondence

$$\hat{P}(\mathbf{b})_j = \left|\varphi(\mathbf{b})_j\right\rangle\!\left\langle\varphi(\mathbf{b})_j\right|.$$