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Excerpt

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## Part 1

# ATOMIC STRUCTURE

# 1

## Development of atomic many-body theory

Ingvar Lindgren

Hugh Padraic Kelly was a pioneer in many-body perturbation theory (MBPT) and its application to atomic systems. He was the first to apply the new diagrammatic technique, developed mainly in field theory and nuclear physics, to problems in atomic physics. He introduced many new ideas, which have been widely used in different areas. In the first years, his work was concerned with the correlation energy of simple atoms and with the hyperfine interaction. In the last two decades he concentrated his efforts on the photoabsorption and photoionization problem, a field where he played a dominant role for a long time. In this chapter I shall give a brief review of the development of atomic MBPT and of the role played by Kelly. I shall also discuss later developments, including relativistic MBPT and QED calculations. I do not intend to give a full account of Kelly's work in different areas, since much of that will be covered in other chapters.

### 1.1 Background

Perturbation theory, which has been used for a long time in mathematical physics and astronomy, was introduced into quantum physics shortly after the advent of quantum mechanics in the 1920s. The most well-known of these schemes are the *Rayleigh-Schrödinger* and the *Brillouin-Wigner* expansions. In principle, these schemes can be used to any order, but they are, in actual atomic and molecular applications, almost prohibitive beyond fourth order, which may be insufficient to achieve the desired accuracy in many cases. During the last decades several new schemes have developed, which make it possible to apply perturbation theory to many-body systems in a more general manner. These schemes have their origin in quantum field theory, which was developed in the late 1940s and in the 1950s by Feynman <sup>[1, 2]</sup> Dyson <sup>[3, 4]</sup> and others.

## 1.1.1 Nuclear MBPT

The technique nowadays usually referred to as *many-body perturbation theory* (MBPT) was first introduced and applied in nuclear physics. The nucleus is a very complex many-body system with strongly interacting particles. In addition, there is no dominant central force, as there is in atomic systems. Nevertheless, it was found – probably to the great surprise of the scientific community – that the nucleus can be well described by a single-particle model in many cases. This is the *nuclear shell model*, proposed in the late 1940s by Goeppert Mayer <sup>[5]</sup> and Jensen *et al.* <sup>[6, 7]</sup> This model was analysed from a many-body point of view by Eden and Francis, <sup>[8]</sup> who introduced fictitious “*quasi-particles*” – distinct from the real nucleons – by means of a “transformed” or “effective” Hamiltonian, similar to that used in modern MBPT.

A particular problem in nuclear physics is the strong repulsive force at short distances between the nucleons, which has the consequence that ordinary perturbation theory cannot be applied. This problem was treated by Brueckner and collaborators in a series of papers in the 1950s. Brueckner and Levinson <sup>[9]</sup> introduced a *reaction operator*, closely related to the scattering matrix used in scattering theory by Lippman and Schwinger <sup>[10]</sup> and Watson. <sup>[11, 12]</sup> In this way an “effective” internucleon force was obtained, which contained the diagonal (“ladder”) part of the true interaction to all orders. The remaining interaction could be handled in a perturbative way. This technique was further developed by Bethe <sup>[13]</sup> and Bethe and Goldstone, <sup>[14]</sup> and the first detailed numerical treatment was performed by Brueckner and Gammel. <sup>[15]</sup>

In a classic paper, Brueckner <sup>[16]</sup> applied the method of Brueckner and Levinson to nuclei with a large number of nucleons (“*nuclear matter*”). He found that the perturbative expansion of the energy contained terms which were *quadratic in the number of nucleons*. When the number of nucleons increases, such terms lead to an energy density, which increases without limit. Hence these terms are unphysical and must be cancelled by other contributions of the expansion. Brueckner called these terms “*reducible*” or “*unlinked*” clusters, since they could be expressed as products of energy contributions of lower order. Considering only two-particle interactions, it is easy to show that the unlinked contributions cancel in the fourth-order energy – the order where they first appear in a nontrivial manner – but Brueckner could, after lengthy calculations, show that they disappear also in the two next higher orders. He conjectured that they should cancel in all orders. This is the *linked-cluster theorem*, which was proved rigorously by Goldstone <sup>[17]</sup> shortly afterwards, using field-theoretical methods. Goldstone showed that the reducible energy clusters of Brueckner were in a diagrammatic description represented by diagrams

which were “*unlinked*,” *i.e.*, which contained two or more disconnected pieces. The theorem is therefore also referred to as the *linked-diagram theorem*. It should be noted that the situation is similar in field theory, where the unlinked diagrams do not contribute to the energy but only to the phase of the wave function.

The first applications of the Brueckner theory were to infinite nuclear matter. It was indicated, however, in several of the papers mentioned above that the method should be applicable also to *finite systems*. The first detailed study of this kind was made by Bethe, <sup>[13]</sup> who showed that the Brueckner theory applied to finite nuclei could form a basis for the nuclear shell model. Of course, for infinite systems, which are translationally invariant, the standard basis functions are the plane-wave solutions of the Schrödinger equation. For finite systems the basis functions are instead solutions in some appropriate external field. To find the “best” field for this purpose is a major problem in the application of MBPT to any finite system. Bethe introduced the idea of starting from self-consistent fields of Hartree-Fock type, and this procedure was further developed by Brueckner *et al.* <sup>[18, 19]</sup> It is not the purpose to discuss here the development of the nuclear many-body theory in any detail. This development serves only as a historical background to the development in atomic physics, which took place later. For reviews on the development of the nuclear applications, the reader is referred to excellent reviews, such as those by Barrett and Kirson <sup>[20]</sup> or Ellis and Osnes. <sup>[21]</sup>

This introductory chapter will be organized in the following way. In the next section the development of atomic many-body perturbation theory will be reviewed, particularly in its non-relativistic formulation. (Relativistic MBPT and QED effects will be treated in the following chapters.) After this introductory review we shall devote the remaining part of the present chapter to an introduction to the diagrammatic formulation of MBPT, based on the Rayleigh-Schrödinger perturbation scheme and to the formalism of second quantization.

## 1.2 Development of atomic MBPT

The first application of MBPT to problems in atomic physics was made by Hugh Kelly in the early 1960s. <sup>[22, 23, 24, 25]</sup> Kelly applied the formalism that was developed by Goldstone. <sup>[17]</sup> The starting point is the many-electron Schrödinger equation

$$H\Psi = E\Psi, \quad (1.1)$$

where  $H$  is the atomic Hamiltonian

$$H = \sum_{i=1}^N h_S(i) + \sum_{i<j=1}^N \frac{1}{r_{ij}}, \quad (1.2)$$

$N$  being the number of electrons, and  $h_S$  being the Schrödinger Hamiltonian for a single electron in the field of the nucleus

$$h_S = -\frac{1}{2}\nabla^2 - \frac{Z}{r}. \quad (1.3)$$

(Hartree atomic units are used throughout this chapter with  $e = m = \hbar = 1$ . See the Appendix.)

The many-electron Hamiltonian is separated in the standard way into an unperturbed Hamiltonian,  $H_0$  and a perturbation,  $V$ ,

$$H = H_0 + V. \quad (1.4)$$

$H_0$  is a sum of single-particle Hamiltonians

$$H_0 = \sum_{i=1}^N h_0(i); h_0 = -\frac{1}{2}\nabla^2 - \frac{Z}{r} + u(r), \quad (1.5)$$

and the perturbation becomes

$$V = \sum_{i<j=1}^N \frac{1}{r_{ij}} - \sum_{i=1}^N u(r_i), \quad (1.6)$$

where  $u$  is some appropriate potential.

The formalism of Goldstone is based on time-dependent perturbation theory, and after performing the time integrations the difference between the total energy  $E$  and the unperturbed energy  $E_0$  can be expressed as a *linked-diagram expansion* (LDĒ)

$$E - E_0 = \Delta E = \sum_{n=0}^{\infty} \left\langle \Phi_0 \left| V \left( \frac{1}{E_0 - H_0} V \right)^n \right| \Phi_0 \right\rangle_{\text{linked}}, \quad (1.7)$$

where  $\Phi_0$  is the unperturbed wave function of the state considered and an eigenfunction of the unperturbed Hamiltonian with the eigenvalue  $E_0$

$$H_0\Phi_0 = E_0\Phi_0. \quad (1.8)$$

The summation in Eq. (1.7) is performed over *linked diagrams*, i.e., diagrams with no disconnected pieces. The wave-function can similarly be expressed

$$\Psi = \sum_{n=0}^{\infty} \left( \frac{1}{E_0 - H_0} V \right)_{\text{linked}}^n \Phi_0. \quad (1.9)$$

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Here also the summation is performed over linked diagrams, but with the term “linked” having a somewhat different definition. In section 1.4 below we shall discuss the LDE in more detail.

The Goldstone formalism is based on *time-ordered* diagrams rather than Feynman diagrams, which contain all possible time-orderings. The term “time-ordered” refers to the time-dependent perturbation formalism and implies that all possible time-orderings between the interactions are represented by separate diagrams.

Of course, for time-independent problems, this classification does not have any physical significance, but it is nevertheless a useful terminology for making a distinction between the two ways treating the perturbations. It can be shown by means of *Wick’s theorem* [26] that for a disconnected diagram all possible time-orderings between the interactions of the separate pieces appear. This leads to the *factorization theorem*, [27] which is useful in proving the linked-diagram theorem starting from Goldstone diagrams, as we shall demonstrate below.

An important ingredient in the MBPT for finite systems, which does not appear for infinite systems, is the *exclusion-principle violation* (EPV). As first stated by Goldstone and emphasized by Kelly, the unlinked diagrams mutually cancel only if the exclusion principle is abandoned in the intermediate states. This leads to additional linked diagrams. For practical applications EPV is an advantage, since the summations over the orbitals can then be performed independently in the different pieces of the diagram. (Among other things, this makes it possible to use the powerful angular momentum technique, developed by Yutsis *et al.* [28]) Kelly found that the EPV diagrams often dominate in higher orders, and he developed several techniques for summing the most important part of these diagrams to all orders.

Kelly’s first application of atomic MBPT was on one of the most well-studied atoms of the periodic table, namely beryllium. [22] The ground state is a closed-shell system,  $1s^2 2s^2$ , and due to the near degeneracy between the  $2s$  and the  $2p$  states, the ground state is strongly correlated. Kelly used a single-electron basis set consisting of bound and unbound states, generated in the Hartree-Fock potential of the ground state. The unbound states were matched to plane-wave solutions at large radii. The calculations were carried out to third-order with some approximations. His result for the correlation energy,  $-0.0920$  a.u., is remarkably good and represents about 97.5% of the correlation energy and compares well with later calculations (see Ref. [29] p. 417, or Refs. [30, 31]). Kelly also found that the higher-order excitations could be even better approximated by a series, which satisfied a simple differential equation. [23, 24] This was one form of what was later called the *independent-pair approximation*. Other related approximations were at about the same time discussed by

Brenig, [32] Nesbet, [33] (also p. 1 of Ref. [34]), Sinanoğlu [35] (also p. 237 of Ref. [34]), and later by Meyer [36] and Kutzelnigg. [37]

The formalism used by Kelly is applicable not only to closed-shell states but also to other systems with non-degenerate unperturbed states. Kelly applied this to evaluate the hyperfine structure of the oxygen atom [38, 39] (also p. 129 of Ref. [34]) and iron. [40] In these cases, Kelly evaluated all second- and third-order and some of the most important fourth-order contributions. The contact parameter obtained for oxygen was within 5% of the experimental value, and the other hyperfine parameters were even closer to the experimental ones.

### 1.2.1 The degeneracy problem

The original MBPT procedure introduced and developed by Brueckner, Goldstone and others was limited to systems with a *non-degenerate* unperturbed state, *i.e.*, essentially closed-shell systems. Early attempts to handle nuclei with open shells were made by Bloch and Horowitz, [41] but their treatment contained some unlinked contributions. A presentation of a fully linked treatment of degenerate (or quasi-degenerate) systems was first made by Brandow [42] and at about the same time by Sandars. [43] Brandow introduced the *folded diagrams* – by Sandars referred to as *backward diagrams* – which are characteristic of open-shell systems.

Brandow's treatment of the linked-diagram expansion is based on the Brillouin-Wigner (BW) expansion, where the *exact* energy of the state considered appears in the energy denominator. This leads to a fairly complicated double expansion. Sandars, on the other hand, based his treatment on the Rayleigh-Schrödinger (RS) expansion, which leads to a simpler structure. Sandars transformed the Schrödinger equation in the following way

$$(E_0 - H_0 - V)\Omega | \Psi_0^a \rangle = - \sum_b \Omega | \Psi_0^b \rangle \langle \Psi_0^b | V \Omega | \Psi_0^a \rangle, \quad (1.10)$$

a form which can be used to generate the RS expansion in a straightforward manner. Essentially the same equation was derived earlier in nuclear physics by Bloch [44]

$$(E_0 - H_0)\Omega \mathbf{P} = V\Omega \mathbf{P} - \Omega \mathbf{P} V \Omega \mathbf{P}, \quad (1.11)$$

an equation nowadays known as the *Bloch equation*.  $\Omega$  is here the *wave operator*, or *Møller operator* [45], which transforms a group of unperturbed wave functions to the corresponding exact ones,  $\Psi^a = \Omega \Psi_0^a$ . (This kind of operator was also used by Eden and Francis, quoted above [8].)  $\mathbf{P}$  is the projection operator for the model space, which is spanned by the unperturbed states,  $\Psi_0^a$ . The Bloch equation is valid when the unperturbed

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states are degenerate (all with the same energy,  $E_0$ ).

Sandars<sup>[43]</sup> proved the LDE for an open-shell system (with a single open shell), starting from Eq. (1.10). He also used the diagrammatic language to find expansions for various effective operators, taking advantage of the powerful graphical angular-momentum technique, introduced by Yutsis *et al.*<sup>[28]</sup> This technique is further exploited and developed in the book by Lindgren and Morrison.<sup>[29]</sup>

The wave operator can be used to define an *effective Hamiltonian*,<sup>[8]</sup> which operating on the unperturbed wave functions yields the corresponding exact energies,  $E^a$ ,

$$H_{\text{eff}} = \mathbf{PH}\mathbf{\Omega}\mathbf{P} ; H_{\text{eff}}\Psi_0^a = E^a\Psi_0^a . \quad (1.12)$$

Hence, the zeroth-order (unperturbed) states are eigenstates of the effective Hamiltonian. (In this formalism the effective Hamiltonian is *non-Hermitian*, which implies that the zeroth-order states are in general non-orthogonal. There exist several modified formalisms, which yield an effective Hamiltonian that is Hermitian.<sup>[46]</sup>)

The Bloch equation (Eq. 1.11), or the equivalent equation used by Sandars (Eq. 1.10), is limited to the situation, where all unperturbed states are exactly degenerate, or, in other words, to atoms with a *single* open shell. In order to be able to treat systems with *several* open shells, it is necessary to generalize the procedure to cover also the case where the model space, which is spanned by the unperturbed states, is not completely degenerate. This was done independently by Lindgren<sup>[47]</sup> and Kvasniča<sup>[48]</sup> and led to a “*generalized Bloch equation*”

$$[\mathbf{\Omega}, H_0] \mathbf{P} = \mathbf{V}\mathbf{\Omega}\mathbf{P} - \mathbf{\Omega}\mathbf{P}\mathbf{V}\mathbf{\Omega}\mathbf{P} . \quad (1.13)$$

This generalized procedure is sometimes referred to as the method with a *multi-reference model space* or somewhat inadvertently as the method with a “quasi-degenerate” model space. It should be noted, however, that the splitting of the model space need not be small. Also large energy differences can be handled, which could appear, for instance, in dealing with inner-hole states. Small energy splittings of the model space, *i.e.*, true quasi-degeneracy, can be handled with the formalism for complete degeneracy by introducing a second perturbation, as demonstrated by Brandow and others.

The Bloch equation is a natural starting point for a formal treatment of MBPT. In the diagrammatic representation the first term,  $\mathbf{V}\mathbf{\Omega}\mathbf{P}$ , contains linked as well as unlinked diagrams. The unlinked diagrams are exactly cancelled by the unlinked part of the second term,  $-\mathbf{\Omega}\mathbf{P}\mathbf{V}\mathbf{\Omega}\mathbf{P}$ , provided the *exclusion principle is abandoned* in the intermediate states. Only linked diagrams remain, including linked EPV diagrams, which is the *linked-*



diagram theorem, [47]

$$[\Omega, H_0] \mathbf{P} = (V\Omega - \Omega P V \Omega)_{\text{linked}} \mathbf{P}. \quad (1.14)$$

The linked part of the second term on the right hand side represents the folded diagrams. This part appears only for open-shell systems. For closed-shell systems, with a single state  $\Phi_0$  in the model space, it is easy to see the connection with the form of the LDE given above (see Eqs. 1.7 and 1.9).

### 1.2.2 The all-order and coupled-cluster approach

The main obstacle in making accurate atomic many-body calculations is usually the slow convergence of the perturbation expansion. Second-order results are often quite good, say within 10%-20% of the correlation, but in order to improve this result significantly it is usually necessary to go to fourth order or beyond. The number of diagrams increases drastically in each order, and a complete fourth-order calculation is monstrous. However, there are several ways of circumventing this problem.

It is well-known that pair-correlations dominate heavily for atomic systems, due to the two-body nature of the basic interaction. The most important higher-order effects appear between the individual pairs of electrons, so-called *intra-pair* correlations. This can be calculated to all orders relatively easily by means of the exact pair equation. In each pair equation, the remaining electrons are passive spectators, contributing only to the average potential. This is the *independent electron-pair approximation* (IEPA), introduced by Sinanoğlu (“exact pair theory”) [35] and Nesbet (“atomic Bethe-Goldstone equation”). [33] This approach is, of course, exact for two-electron systems, but in order to improve the accuracy for many-electron systems, it is necessary to take into account – at least approximately – also the *inter-pair* correlation, *i.e.*, the interaction between different pairs of electrons.

Higher-order diagrams of a certain class can also be generated by an *iterative procedure*. This was first demonstrated for single excitations (core polarizations) [49] and first applied to the pair-correlation problem by Mårtensson. [50] By solving a set of coupled one- and two-electron equations, it is possible in this way to include the effects of single and double excitations to all orders of perturbation theory. [51] Single excitations are less important for closed-shell systems, due to the Brillouin theorem, but they are still significant when high accuracy is desired. [30, 51, 52] For open-shell systems, on the other hand, single-excitations are of vital importance and have to be included at every level of accuracy. The starting point for open-shell atomic MBPT calculations is usually the Hartree-Fock (HF) solution for a closed-shell state or some local potential, which includes the

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valence electrons in an averaged way. In neither case is the Brillouin theorem valid. Therefore, for open-shell systems single excitations appear in the second-order energy, while for closed-shell systems, using HF orbitals, they appear first in the fourth order.

It should be noted here that considering certain excitations (singles and doubles, say) in the linked-diagram expansion is *not* equivalent to considering such excitations using the original Schrödinger equation – or the Bloch equation, which is just a rewriting of the latter. This is due to the fact that, for instance, the cancellation of unlinked diagrams with double excitations in the last term of the Bloch equation,  $-\Omega P V \Omega P$ , requires *quadruple* excitations in the first term,  $V \Omega P$ . As a consequence, an all-order linked-diagram expansion with singles and doubles is not exact for the helium atom! Also some quadruple excitations of EPV type are needed. In the exact pair equation, the corresponding contribution is, of course, correctly included.

For many-electron systems, *true* quadruple excitations (not of EPV type) are quite important. They may represent several percent of the total correlation and are usually more important than triple excitations. The dominant quadruple excitations are of a special kind, which can be regarded as two independent double excitations. Such excitations can be included in a pair-correlation approach by expressing the wave operator in the form  $\Omega = 1 + S + \frac{1}{2}S^2$ , as first noted by Sinanoğlu. [35] A double excitation in  $S$  will then generate the dominating quadruple excitations in  $\Omega$  due to the quadratic term. A generalization of these arguments leads to the “*exponential ansatz*” or *exp(S) formalism*, where the wave operator is expressed in exponential form

$$\Omega = e^S = 1 + S + \frac{1}{2}S^2 + \frac{1}{3!}S^3 + \dots \quad (1.15)$$

This approach is nowadays usually referred to as the *coupled-cluster approach* (CCA),  $S$  being the “cluster” operator.

The exponential ansatz has its roots in statistical mechanics and was introduced into nuclear physics in the late 1950’s by Hubbard [53] and Coester and Kümmel. [54] (See also the review article by Kümmel *et al.* [55]) The procedure was introduced by Čížek [56] (also p. 35 of Ref. [34]) into quantum chemistry – a field where it has been widely used for many years. [57]

The CCA with singles and doubles combines the advantages of the standard LDE of being a good approximation for large systems and of the exact or independent pair approach of being exact for two-electron systems. For typical atoms it is possible to reach a 99% level of accuracy for the correlation energy with this approximation. [51, 57]

The advantage of CCA compared to standard MBPT is particularly