

Electron correlation and quantum electrodynamics†

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A review is given of the coupled-cluster approach for a multi-reference model space. Various schemes of normalization are discussed, particularly the hermitian formulation. Relativistic many-body schemes are analysed, starting from the no-virtual-pair approximation (NVPA). Effects beyond NVPA are discussed in the framework of QED, and in particular the QED effects on the electron correlation for He-like ions are analysed.

1. Introduction

Non-relativistic many-body procedures have been extensively used over the past 40 years and can now be regarded as well developed. The important *linked-diagram expansion* (LDE) was discovered by Brueckner and Goldstone [1] in the middle of the 1950s. The advent of LDE represented a great progress in the many-body procedure and is normally regarded as the starting point of *many-body perturbation theory* (MBPT). In the 1960s the procedure was further developed for open-shell systems by Brandow, Sandars, Kelly and others and later also for quasi-degenerate or general multi-reference model space [2]. In an order-by-order expansion, like LDE, however, the number of terms increases drastically with the order, and this has the consequence that the method becomes essentially intractable for open-shell systems beyond the third-order energy.

Instead of an order-by-order expansion it is often more efficient to treat certain effects—like one- and two-particle effects—to all orders in a recursive manner. A particularly useful version of such a procedure is the *coupled-cluster approach* (CCA), where the wavefunction (or wave operator) is expressed in exponential form. This approach was developed in nuclear physics by Coester and Kümmel [3] and introduced into quantum chemistry by Cizek in the 1960s [4]. It was first developed and applied to closed-shell systems [5] and in the 1970s extended to open-shell systems and general multi-reference model space [6].

The multi-reference CCA (MR-CCA) is a very clean procedure with many nice features. It satisfies the important *size-extensivity* criterion for the energy and also the *separability* or *size consistency* condition for the wavefunction [5 (b), 5 (c), 7]. In the MR-CCA it is—at least in principle—possible to include important mixing states into the model space, which will improve the accuracy

and speed up the convergence of the iterations. However, the original formulation was limited to a *complete model space*. In practical applications such a space can be quite large, with the consequence that *intruder states* [8] destroying the convergence of the procedure, are very likely to appear.

A well-known classical example of the intruder problem is the Be atom. With the orbitals generated in the HF potential of the $1s^2$ the core, the configurations $1s^2 2s^2$ and $1s^2 2p^2$ are closely degenerate and strongly mixed. An extended model space with the two configurations contains two 1S states, of which the upper one is very highly excited, in fact above the $2s$ ionization limit. This means that there is an infinite number of other 1S states (from the $1s^2 2s n s$ configurations) which will fall between the states originating from the model space. It was earlier observed that the standard CC procedure does not converge in this situation [9]. Later, it has been possible to circumvent the intruder problem in this special case by means of special tricks [10].

Normally, one is interested in only a limited number of states originating from a complete model space—usually some low-lying states—and it would then be desirable to work with a more limited model space in order to reduce the intruder problem. However, the CC procedures were until recently developed only for complete model spaces. For an incomplete model space the standard MR-CCA procedure with *intermediate normalization* (IN) generally leads to *disconnected* cluster operators and loss of size extensivity. It was first pointed out by Mukherjee and co-workers [11] that connectivity could be restored for very general incomplete model spaces by abandoning the IN. This opened up quite new possibilities and turned out to be one effective way of handling the intruder problem in MR-CCA.

Another way of handling the intruder problem is the *intermediate hamiltonian approach*, developed by

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Malrieu, Durand and others [12] Here, only a few of the eigenstates of the effective hamiltonian correspond to real states. This may give sufficient freedom in constructing that hamiltonian so that the intruder problem could be avoided.

It is also possible to construct a ‘*state-specific*’ procedure, which is size extensive, as recently demonstrated by Mukherjee and co-workers [13]

Relativistic many-body procedures were not developed until the 1980s. Relativistic SCF procedures (MCDF) were used already in the 1970s but based on a non-rigorous hamiltonian [14]

Breit had derived already around 1930 the relativistic corrections to the Coulomb interaction [15] The original Breit interaction, however, could be used only in first order and was not suitable for many-body procedures. It was demonstrated by Brown and Ravenhall [16] in the early 1950s that a relativistic hamiltonian based upon the Coulomb interaction (with or without the Breit interaction) has eigenvalues that are not bound from below, due to the presence of the negative energy states. The problem with the Breit interaction was further emphasized by Bethe and Salpeter [17] and this did for a long time hamper the use of the Breit interaction in many-body applications.

It was demonstrated by Sucher in 1980 [18] that the problem with negative energy states could be avoided by the use of *projection operators*. This leads to the so-called *no-virtual-pair approximation* (NVPA). In this scheme it is perfectly legitimate to iterate also the Breit interaction to self-consistency. There are other effects (*‘QED effects’*) that are of the same order as the second-order Breit interaction, but the important point here is that the Breit interaction could be treated on the same footing as the Coulomb interaction without any fear of ‘falling into the Dirac sea’.

Relativistic effects are intimately connected to *quantum electrodynamics* (QED), and an analysis of the relativistic many-body problem must by necessity start from QED. It turns out that such an analysis yields an interelectronic interaction that is *gauge dependent*. SCF calculations performed with the interactions derived using, for instance, the Coulomb and the Feynman gauges turned out to yield significantly different results, and this caused confusion for some time [19]

In order to resolve the problem with the interelectronic interaction, it is necessary to consider also the *two-photon exchange* between the electrons (see figure 4, section 3.2). It was then demonstrated that the gauge dependence could be explained to first order by the effects left out of the two-photon exchange [20] For instance, the crossed-photon diagram, entirely left out in any many-body procedure developed so far, is an order

of magnitude larger in the Feynman gauge than in the Coulomb gauge. In fact, the Coulomb gauge turns out to be the optimum gauge for many-body applications, and this gauge leads (in the no-retardation limit) exactly to the original Breit interaction.

The NVPA, based upon the Coulomb gauge with the Coulomb and the Breit interactions, is a very efficient computational procedure for atomic and molecular systems that are not highly charged. It has in recent years been applied by several groups, particularly to atomic problems [21]

The effects left out in NVPA are referred to as *QED effects*. These are of two kinds: (a) *non-radiative effects* (sometimes referred to as the Araki–Sucher effect [22]) and (b) *radiative effects*. The former are caused by the negative energy states and the retardation effects left out in NVPA. The radiative effects are of Lamb-shift type and involve self energy and vacuum polarization.

For highly charged systems the single-electron Lamb shift can be comparable to the first-order Breit interaction. Since it is a single-particle effect, however, it has no effect upon the electron correlation. The non-radiative effects and the higher-order Lamb shift, on the other hand, do have such effects. This has recently been studied for He-like ions [23] and compared with experimental results [24] The experimental accuracy is not yet sufficient for detecting the effects, but with only a moderate improvement of the accuracy a significant test will be possible. This will constitute an important test of QED (beyond first-order Lamb shift) at very strong fields.

In the present paper we shall in section 2 review some recent developments in the non-relativistic CC theory, particularly regarding incomplete model space and the hermitian formulation. Some new results will be reported. In section 3 we shall first analyse the gauge dependence of the electron–electron interaction in the NVPA, and finally the QED effects upon the electron–electron interaction will be discussed and some new results for He-like ions be reported.

2. Non-relativistic many-body theory

2.1. Multi-reference model space

As a background for the following treatment and for defining our notations, we will first briefly review the well-known non-relativistic many-body theory for a general multi-reference model space. We shall apply the Bloch formalism, which yields a transparent relation between different formulations [2(i)]

We start from the Schrödinger equation for a number of states (target states),

$${}_H \Psi^{(a)} = E^{(a)} \Psi^{(a)} \quad (a = 1, 2, \dots, d), \quad (1)$$

where H is the hamiltonian and Ψ is the wavefunction of the system. The corresponding *zeroth-order wavefunctions* (ZOWF), $\Psi_0^{(a)}$, are confined to a *model space*, P , which might contain several zeroth-order energies (multi-reference model space). If the model space contains all possible occupancies of the valence orbitals, it is said to be *complete*, but the treatment here holds for a general, *incomplete* model space. (For a more extensive discussion about the incomplete-model-space problem, see e.g. the review by Lindgren and Mukherjee [11 (d)]).

We assume that a *wave operator* (W) transforms all ZOWF into the corresponding exact wavefunctions,

$$\Psi^{(a)} = \Omega \Psi_0^{(a)} \quad (a = 1, 2, \dots, d). \quad (2)$$

The ZOWF are eigenfunctions of an *effective* or *model hamiltonian*, H_{eff} , with eigenvalues equal to the exact energies

$$H_{\text{eff}} \Psi_0^{(a)} = E^{(a)} \Psi_0^{(a)} \quad (a = 1, 2, \dots, d). \quad (3)$$

The explicit form of this operator depends on the normalization scheme employed (see below).

For the following we shall partition the hamiltonian into an unperturbed hamiltonian, H_0 , and a perturbation, V ,

$$H = H_0 + V, \quad (4)$$

and we define a corresponding *effective interaction*, V_{eff} , by

$$V_{\text{eff}} = H_{\text{eff}} - P H_0 P. \quad (5)$$

The wave operator satisfies the generalized Bloch equation [2 (g)–2 (i)]

$$[\Omega, H_0] P = (V \Omega - \Omega V_{\text{eff}}) P, \quad (6)$$

where P is the projection operator of the model space. In *intermediate normalization* (IN) we have

$$\begin{aligned} \Psi_0^{(a)} &= P \Psi^{(a)}; \quad P \Omega P = P; \\ H_{\text{eff}} &= P H \Omega P \quad \text{and} \quad V_{\text{eff}} = P V \Omega P. \end{aligned} \quad (7)$$

Other normalization schemes are discussed below.

2.2. The linked-diagram expansion

In the standard perturbation theory the wave operator is expanded order by order,

$$\Omega = \Omega^{(0)} + \Omega^{(1)} + \Omega^{(2)} + \dots \quad (8)$$

[$X^{(0)} = 1$ in IN] Inserting this expansion into the generalized Bloch equation (6) yields

$$[\Omega^{(n)}, H_0] P = (V \Omega - \Omega V_{\text{eff}})^{(n)} P. \quad (9)$$

This equation leads to the general Rayleigh–Schrödinger (RS) expansion for a multi-reference model space.

In the diagrammatic representation the RS expansion contains ‘*unlinked*’ diagrams, i.e. diagrams with a disconnected, closed part. Such diagrams can be shown to cancel, which leads to the *linked-diagram expansion* (LDE) [1, 2]. The LDE can then be expressed by means of a ‘modified Bloch equation’

$$[\Omega, H_0] P = (V \Omega - \Omega V_{\text{eff}})_{\text{linked}} P \quad (10)$$

with the order-by-order expansion

$$[\Omega^{(n)}, H_0] P = (V \Omega - \Omega V_{\text{eff}})_{\text{linked}}^{(n)} P. \quad (11)$$

This form of the perturbation theory is very convenient for generating the LDE. The term ΩV_{eff} represents the *folded* or *backwards* diagrams [2 (a), 2 (f)]

The order-by-order expansion is usually impractical beyond the third-order energy due to the large number of diagrams appearing. For many atomic and molecular systems, which are not highly charged, however, third order is often insufficient, and more efficient methods have been developed.

2.3. The all-order and coupled-cluster approaches

Instead of an order-by-order expansion (8) we separate the wave operator into zero-, one-, two-, ... body terms, defined by means of second-quantization,

$$\begin{aligned} \Omega &= \Omega_0 + \Omega_1 + \Omega_2 + \dots = \Omega_0 + \sum_{ij} x_j^i \{a_i^\dagger a_j\} \\ &+ \frac{1}{2} \sum_{ijkl} x_{kl}^{ij} \{a_i^\dagger a_j^\dagger a_l a_k\} + \dots \end{aligned} \quad (12)$$

Solving the corresponding partitions of the Bloch equation iteratively to self-consistency,

$$[\Omega_n, H_0] P = (V \Omega - \Omega V_{\text{eff}})_{n, \text{linked}} P, \quad (13)$$

is equivalent to treating the corresponding effects to *all orders of perturbation theory*.

In the LDE all energy or effective-hamiltonian diagrams are *connected*. The wave-operator expansion, on the other hand, also contains disconnected diagrams with open pieces. For a single-reference model space such diagrams factorize into an ordinary product of connected diagrams. This can be generalized to the *exponential Ansatz* or *coupled-cluster approach* (CCA) [3]

$$\Omega = \exp S = 1 + S + \frac{1}{2!} S^2 + \frac{1}{3!} S^3 \dots, \quad (14)$$

where the ‘*cluster operator*’ S is completely connected [4, 5]

For open-shell systems (multi-reference model space) the disconnected diagrams factorize into a normal-ordered rather than an ordinary product. This leads to

the *normal-ordered exponential Ansatz*, proposed independently by Lindgren [6(c)] and Ey [6(e)]

$$\Omega = \{\exp s\} = 1 + s + \frac{1}{2!} \{s^2\} + \frac{1}{3!} \{s^3\} \dots \quad (15)$$

The cluster operator is under general conditions completely connected also in this case and satisfies an equation, which is quite analogous to the wave-operator equations (6) and (10),

$$[\mathcal{S}, H_0]P = (V\Omega - \Omega V_{\text{eff}})_{\text{conn}} P. \quad (16)$$

For the following we shall make the assumption of *valence universality*, which implies that the wave operator introduced above transforms the wave functions for all valence sectors, m , i.e. for all systems with one or several valence electrons removed or one or several valence holes filled (or any combination thereof). The Bloch cluster equation (16) is then extended to

$$[\mathcal{S}, H_0]P^{(m)} = (V\Omega - \Omega V_{\text{eff}})_{\text{conn}} P^{(m)}, \quad (17)$$

for all sectors m . Here $P^{(m)}$ is the projections operator for the model space of the valence sector m . The assumption of valence universality makes the cluster operator uniquely defined by the Bloch-type equation, and it leads to connectivity, using general normalization schemes [11(c), 11(d)]

Expanding the cluster operator in analogy with the wave-operator (12) and truncating after the two-body term

$$s = s_1 + s_2 \quad (18)$$

leads to the frequently used CCSD approximation. The coupled one- and two-electron equations are in this approximation [2(i), 6(c)]

$$[\mathcal{S}_{1, H_0}]P^{(m)} = \left\{ v + v s + \frac{1}{2} v s_1^2 + v s_1 s_2 + \dots - s_1 V_{\text{eff}, 1} \right\}_{1, \text{conn}} P^{(m)}, \quad (19a)$$

$$[\mathcal{S}_{2, H_0}]P^{(m)} = \left\{ v + v s + \frac{1}{2} v s_1^2 + v s_1 s_2 + \frac{1}{2} v s_2^2 + \dots - s_2 V_{\text{eff}, 2} - \dots \right\}_{2, \text{conn}} P^{(m)}. \quad (19b)$$

2.4. Incomplete model space

The most frequently used normalization scheme in many-body theory is the *intermediate normalization* (IN) (7), which works well for a complete model space. Such a model space, however, can in realistic applications be impractically large and may likely lead to *intruder states* [8] which destroy the convergence of the perturbation expansion.

In most cases only a limited number of states within a complete model space are of interest for the problem at hand. One way to avoid—or at least reduce—the

intruder problem is then to restrict the model space, and work with an *incomplete model space*. In such a scheme, however, the connectivity or size extensivity cannot be guaranteed, when the IN is employed. It was first demonstrated by Mukherjee and co-workers [11] that connectivity and size extensivity can be generally restored for an incomplete model space by abandoning the IN.

Introducing the inverse of the wave operator, operating to the left on the model space, leads to

$$P^{(m)} \Omega^{-1} \Omega P^{(m)} = P^{(m)} \quad (20)$$

instead of the IN relation (7) $P^{(m)} \Omega P^{(m)} = P^{(m)}$. The effective hamiltonian then becomes

$$H_{\text{eff}}^{(m)} = P^{(m)} \Omega^{-1} H \Omega P^{(m)}. \quad (21)$$

In IN the effective interaction to be used in the CC Bloch equation (16) can be given an explicit form (6). This is not the case with a general normalization scheme. Instead, we have here to consider the Q as well as the P projections as coupled equations and solve them iteratively [11(d)]

$$Q^{(m)} [\mathcal{S}, H_0]P^{(m)} = Q^{(m)} (V\Omega - \chi V_{\text{eff}})_{\text{conn}} P^{(m)} \quad (22a)$$

$$P^{(m)} [\mathcal{S}, H_0]P^{(m)} = P^{(m)} (V\Omega - \Omega V_{\text{eff}})_{\text{conn}} P^{(m)} \quad (22b)$$

with $\chi = \Omega - 1$. From the P projection we get an implicit expression for the effective interaction

$$V_{\text{eff}}^{(m)} = P^{(m)} (V\Omega - \chi V_{\text{eff}}^{(m)} - [\mathcal{S}, H_0]_{\text{conn}}) P^{(m)}. \quad (23)$$

There are other ways of handling the intruder problem, such as the *intermediate-hamiltonian* (IH) formalism, introduced by Malrieu, Durand and co-workers [12] Here, the effective hamiltonian is defined in such a way that it reproduces the exact energies only for a subgroup of the target states. With this technique one can utilize the larger model space with its good representation of the ZOWF and simultaneously to a large extent avoid the intruder problem. Other schemes are focusing on a single state of a multi-reference model space, *state-specific methods*, as recently analysed by Mukherjee and co-workers [13] We shall not consider these schemes any further here, since they will be the subject of special talks later at this workshop.

2.5. Hermitian formulation

The IN (as well as several other schemes) also has the disadvantage that the effective hamiltonian is *non-hermitian*. Several hermitian schemes have been developed and applied in many-body theory [25] We shall particularly consider the scheme of Jørgensen [26] Here, the normalization condition is

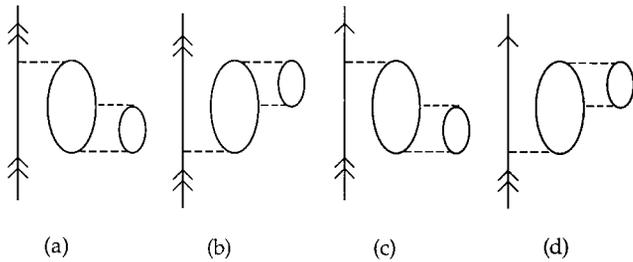


Figure 1. In the standard pair-correlation (CCSD) approach (19), the effective-operator diagram (a) would be generated in intermediate normalization but not the corresponding hermitian adjoint diagram (b). Similarly, the wave-operator diagram (c) would be included but not the analogous diagram (d), which involves a triple excitation. In the ‘symmetrized’ hermitian formulation (29) all these diagrams would be included in the CCSD approach.

$$P^{(m)} = P^{(m)} \Omega^\dagger \Omega P^{(m)}. \quad (24)$$

and the effective hamiltonian becomes

$$H_{\text{eff}}^{(m)} = P^{(m)} \Omega^\dagger H \Omega P^{(m)}, \quad (25)$$

which is manifestly hermitian. It has been shown by Lindgren [25(d)] that connectivity is preserved in the CCA also in this scheme.

The non-hermiticity caused by IN leads to an asymmetry in the representation at a particular level, which can be illustrated by the diagrams in figure 1. In the CCSD procedure (19), where only single and double excitations are considered in the cluster operator (with no passive valence orbital), diagram (a) will be included but not its hermitian adjoint (b). The reason for this is that the corresponding wave-operator diagram (d) contains a triple excitation, before it is closed.

Even with the Jørgensen condition (24), however, non-hermiticity can be introduced by *truncations*. The general equation for the effective interaction (23) leads obviously with the Jørgensen condition to hermiticity, when *all* effects are included, but not necessarily so for a truncated expansion [25(d)].

In order to improve hermiticity for truncated expansions, following the procedure of Lindgren in [25(d)], we shall develop more symmetric expressions by operating on the CC Bloch equation (17) with Ω^\dagger from the left,

$$\Omega^\dagger [\mathcal{S}, H_0] P^{(m)} = \Omega^\dagger (V \Omega - \Omega V_{\text{eff}}^{(m)})_{\text{conn}} P^{(m)}. \quad (26)$$

Using $\chi = \Omega - 1$, this leads to the P and Q projected equations

$$\begin{aligned} Q [\mathcal{S}, H_0] P^{(m)} &= Q (V \Omega - \Omega V_{\text{eff}}^{(m)} + \chi^\dagger (V \Omega - \Omega V_{\text{eff}}^{(m)} \\ &\quad - [\mathcal{S}, H_0])_{\text{conn}} P^{(m)} \end{aligned} \quad (27)$$

$$\begin{aligned} V_{\text{eff}}^{(m)} &= P^{(m)} (V \Omega - \chi V_{\text{eff}}^{(m)} - [\mathcal{S}, H_0] \\ &\quad + \chi^\dagger (V \Omega - \Omega V_{\text{eff}}^{(m)} - [\mathcal{S}, H_0])_{\text{conn}} P^{(m)}. \end{aligned} \quad (28)$$

The extra terms, compared to (22) and (23), vanish, when *all* effects are considered, but not necessarily so for truncated expansions. The extra terms may improve the hermiticity for truncated schemes, as will be illustrated below.

In the expressions (27) and (28) large cancellations occur between the terms of the right-hand side, and a more convenient way of expressing the relations is

$$\begin{aligned} Q [\mathcal{S}, H_0] P^{(m)} &= Q (V \Omega - \Omega V_{\text{eff}}^{(m)} \\ &\quad + \chi^\dagger (V \Omega - \Omega V_{\text{eff}}^{(m)})_{+})_{\text{conn}} P^{(m)} \end{aligned} \quad (29a)$$

$$\begin{aligned} V_{\text{eff}}^{(m)} &= P^{(m)} (V \Omega - \chi V_{\text{eff}}^{(m)} - [\mathcal{S}, H_0] \\ &\quad + \chi^\dagger (V \Omega - \Omega V_{\text{eff}}^{(m)})_{+})_{\text{conn}} P^{(m)}, \end{aligned} \quad (29b)$$

where the + sign represents effects with the intermediate state outside the approximation employed [25(d)].

The extended expressions (29) reduce the non-hermiticity also with other normalizations, such as the IN. This can be illustrated by means of the diagrams in figure 1. Also with the extension terms the diagrams (b) and (d) will in the CCSD approximation be included in the effective hamiltonian and the wave operator, respectively. The importance of the hermitian extension terms was demonstrated in an early calculation on the sodium atom by Salomonson and Ynnerman [27].

The inclusion of the hermitian extension terms lead to a systematic extension of the CC equations. This is illustrated with the single-particle equation. In the case of a passive valence orbital it can be shown that the extended equations (29) in the IN lead to the complete *random-phase approximation* (RPA), with forward and backward loops, while the standard procedure only leads to the *Tamm-Dankoff approximation* (TDA) with only forward loops (see figure 2) [25(d)].

The hermitized CC procedure has recently been applied by Salomonson *et al.* [28] in a calculation of the electron affinity of the Ca and Sr atoms. The binding of the last electron of the negative ion is here very delicate, and it is only recently that this quantity has been reliably measured [29]. The corresponding theoretical evaluation has also for a long time challenged the theo-

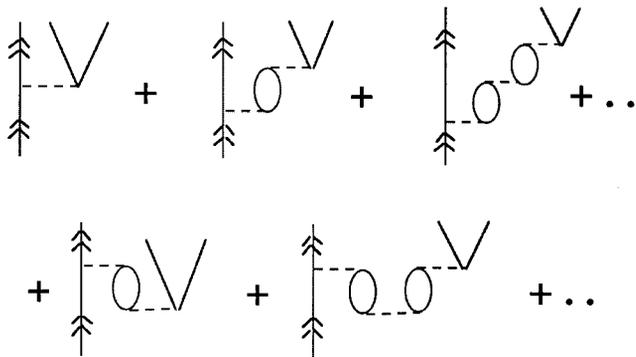


Figure 2. The diagram of the first row with forward loops only are generated in the single-electron approximation (with a passive valence orbital) in the standard CCA. The second-row diagrams with backward loops are generated by the extension terms in (29). This represents the complete *random-phase approximation* (RPA).

reticians [30] The technique used by Salomonson *et al.* is based on the quasi-particle equation

$$h_{\text{HF}}\varphi(\mathbf{r}) + \int d^3r' \Sigma^*(\mathbf{r}, \mathbf{r}', \varepsilon)\varphi(\mathbf{r}') = \varepsilon\varphi(\mathbf{r}) \quad (30)$$

with an energy-dependent self-energy potential, $\Sigma^*(\mathbf{r}, \mathbf{r}', \varepsilon)$, evaluated by means of the CC procedure,

$$\begin{aligned} \Sigma^*(\mathbf{r}, \mathbf{r}', \varepsilon) = & \langle \mathbf{r}' | P (V_2 S_2 + V_2 S_1 + S_1^\dagger V_2 \\ & + S_2^\dagger (V_2 S_2)_+) |_{\varepsilon, \text{conn}} P | \mathbf{r} \rangle \end{aligned} \quad (31)$$

The rhs depends on the energy (ε) of the valence orbital, and equations (30) and (31) are iterated until self-consistency is reached. This procedure yields for the first time good agreement with the experimental results for Ca^- as well as Sr^- [28]

3. Relativistic many-body theory and QED

3.1. No-virtual-pair approximation

For relativistic many-body calculations a frequently used hamiltonian is the *Dirac-Coulomb hamiltonian*

$$H = \sum h_{\text{D}} + \sum_{r_{ij}} \frac{1}{r_{ij}}, \quad (32)$$

where the single-electron Schrödinger hamiltonian, h_{S} , of the standard non-relativistic hamiltonian is replaced by the corresponding Dirac hamiltonian

$$h_{\text{D}} = c\alpha \cdot \mathbf{p} + \beta m c^2 - \frac{Z}{r} \quad (33)$$

(using Hartree atomic units, $e = m = \hbar = 4\pi\epsilon_0 = 1$). This hamiltonian has been used, for instance, for a long time in multi-configuration Dirac-Fock (MCDF) calculations [14] and to some extent also in relativistic MBPT calculations. The eigenvalues of this hamiltonian, how-

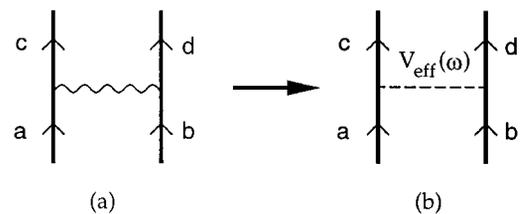


Figure 3. The exchange of a single photon between two electrons (a) is compared with an effective-potential interaction (b).

ever, are not bound from below, with the consequence that the eigenstates may dissolve into the negative continuum [16]

A more rigorous basis for relativistic many-body work is the *projected hamiltonian* [18]

$$H = \Lambda_+ \left(\sum h_{\text{D}} + \sum V_{ij} \right) \Lambda_+, \quad (34)$$

where Λ_+ is the projection operator for positive-energy states, which prevents the negative-energy states from entering into the wave function. This is the *no-(virtual)-pair approximation* (NVPA), in which virtual electron-positron pairs are not allowed in intermediate states.

With the form (34) of the Hamiltonian it is relatively straightforward to set up a relativistic CC procedure, following the non-relativistic procedure outlined in the previous section. This has been done by various groups during the last 5–8 years [21]

The form of the interelectronic potential, V_{ij} , can be derived from QED, but unfortunately it turns out that this depends on the gauge used, and it is not obvious which potential is the best to use in relativistic many-body theory. In the next section we shall analyse this problem by considering the one- and two-photon exchange between the electrons.

3.2. One- and two-photon exchange

We consider first the exchange of a single photon between the electrons, represented by the Feynman diagram in figure 3(a). We employ *bound-state QED* with the field operators

$$\Psi = \sum a_i \phi_i(x); \quad \Psi^\dagger = \sum a_i^\dagger \phi_i^*(x) \quad (35)$$

and the orbitals generated in the external (nuclear) field, $v(x)$, (Furry picture [31])

$$\left[c\alpha \cdot \mathbf{p} + \beta m c^2 + v(x) \right] \phi(x) = \varepsilon \phi(x). \quad (36)$$

The S -matrix for the single-photon exchange (figure 3(a)) then becomes

$$\begin{aligned} \langle cd | S^{(2)} | ab \rangle &= -2\pi i \delta(\varepsilon_a + \varepsilon_b - \varepsilon_c - \varepsilon_d) \\ &\times \langle cd | a_1^\mu \alpha_2^\nu e^2 D_{F\nu\mu}(\mathbf{x}_2 - \mathbf{x}_1, \omega) | ab \rangle, \end{aligned} \quad (37)$$

where $D_{F\nu\mu}(\mathbf{x}_2 - \mathbf{x}_1, \omega)$ is the Feynman photon propagator and $a^\mu = (1, -\mathbf{a})$ the Dirac operators in covariant form. The expression (37) can be compared with the corresponding expression for single potential scattering (figure 3(b))

$$\langle cd | S^{(1)} | ab \rangle = -2\pi i \delta(\varepsilon_a + \varepsilon_b - \varepsilon_c - \varepsilon_d) \langle cd | V_{\text{eff}}(\omega) | ab \rangle, \quad (38)$$

which leads to the ‘effective’ interaction potential

$$V_{\text{eff}}(\omega) = \alpha_1^\mu \alpha_2^\nu e^2 D_{F\nu\mu}(\mathbf{x}_2 - \mathbf{x}_1, \omega). \quad (39)$$

This potential is *energy dependent*, through the energy parameter ω , representing the energy transfer of the photon, and—as mentioned earlier—it is also *gauge dependent*.

We consider particularly two gauges, the *Feynman* and the *Coulomb* gauges. In these gauges the unretarded or frequency-independent part of the interaction becomes

$$V_{\text{eff}}^F(\omega = 0) = \frac{1}{r_{12}} (1 - \alpha_1 \cdot \alpha_2) \quad (40a)$$

$$V_{\text{eff}}^C(\omega = 0) = \frac{1}{r_{12}} \left(1 - \frac{1}{2} \alpha_1 \cdot \alpha_2 - \frac{(\alpha_1 \cdot \mathbf{r}_{12})(\alpha_2 \cdot \mathbf{r}_{12})}{2r_{12}^2} \right), \quad (40b)$$

known as the *Coulomb–Gaunt* and *Coulomb–Breit* interactions, respectively.

In principle, the results of QED are gauge independent in each order. Nevertheless, it has been found that the interactions derived with the two gauges (even with retardation included) lead to significantly different results, when used in SCF or MBPT calculations [19]. The single-photon exchange in QED, however, involves *energy conservation* (37), and the potential derived is therefore strictly valid only for evaluating the *first-*

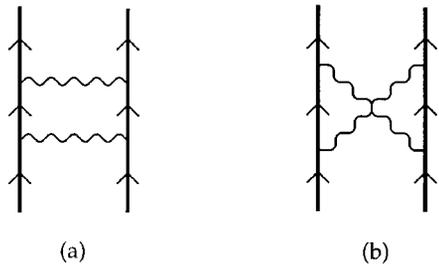


Figure 4. Two two-photon exchange between the electrons is represented by two Feynman diagrams, (a) the ‘ladder’ and (b) the ‘crossed-photon’ diagram.

order energy contribution (in which case the two gauges yield identical results). When the potential is used iteratively in many-body procedures, on the other hand, gauge dependence appears. In order to analyse the gauge dependence, it is then necessary to consider the *two-photon exchange* (figure 4).

In a many-body procedure, where a single-photon potential of the type (40) is used iteratively, the crossed-photon diagram is left out completely and the ladder diagram is only partly included. It can be shown that the parts left out are much more important in the Feynman gauge than in the Coulomb gauge. Therefore, the potential derived in the latter gauge yields more accurate results in a many-body procedure. In fact, the Coulomb-gauge potential leads to errors of the order of α^3 hartrees, while most other gauges would cause errors of the order of α^2 hartrees. This leads to the recommended *no-virtual-pair approximation* (NVPA)

$$H = \Lambda_+ \left(\sum h_D + \sum \left(\frac{1}{r_{ij}} + B_{ij} \right) \right) \Lambda_+, \quad (41a)$$

where

$$B_{12} = -\frac{1}{2r_{12}} \left(\alpha_1 \cdot \alpha_2 + \frac{(\alpha_1 \cdot \mathbf{r}_{12})(\alpha_2 \cdot \mathbf{r}_{12})}{r_{12}^2} \right) \quad (41b)$$

is the Breit interaction (40b), representing the first-order magnetic interaction and retardation of the (instantaneous) Coulomb interaction.

Table 1. Two-electron contribution to the ground-state energy of He-like ions. Comparison between theory and experiment (in eV).

Nuclear charge	MBPT			Non-radiative	Lamb shift	Total theory	Experimental Marrs <i>et al.</i>
	First order	2nd	3rd				
32	567.1	- 5.22	0.02	0.03	- 0.42	562.02 (10)	562.6 ± 1.6
54	1036.56	- 7.04	0.03	0.16	- 1.56	1028.15 (10)	1027.2 ± 3.5
66	1347.45 (1)	- 8.59	0.03	0.36	- 2.66	1336.59 (10)	1341.5 ± 4.3
74	1586.93 (2)	- 9.91	0.04	0.55	- 3.68	1573.93 (10)	1568.9 ± 15
83	1897.56 (4)	- 11.77	0.04	0.86	- 5.16	1881.5 (2)	1875 ± 14
92	2265.87 (10)	- 14.16	0.05	1.28	- 7.12	2245.9 (2)	

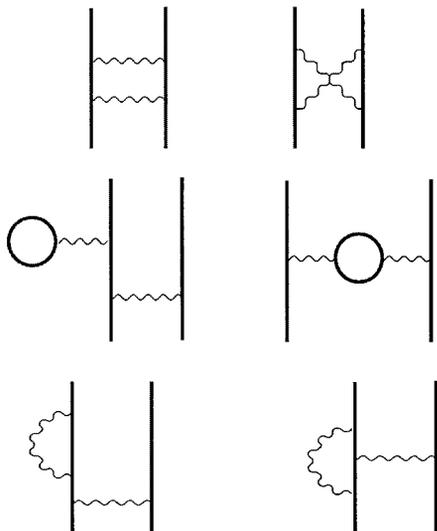


Figure 5. Feynman diagrams of the second-order two-electron contribution to the binding energy of He-like systems. The first line represents the many-body part and the non-radiative QED part, and the remaining lines the radiative contribution (screening of the Lamb shift).

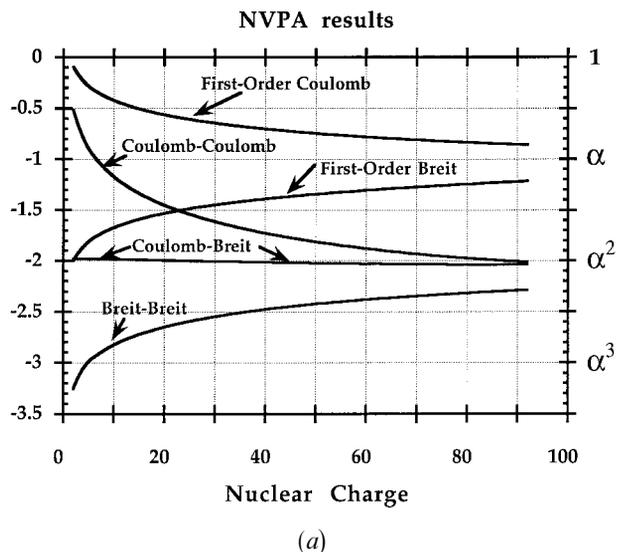
The NVPA in the Coulomb gauge is nowadays the standard approximation for relativistic many-body calculations. It forms the basis for the modern versions of the MCDF procedures [19(a), 19(b), 32] and has been employed in MBPT and coupled-cluster calculations [21]

3.3. QED effects

The effects left out in the NVPA are defined as QED effects. They are of two types:

- (a) *non-radiative effects*, i.e. effects of retardation and of negative-energy states,
- (b) *radiative effects*, i.e. self-energy and vacuum-polarization or Lamb-shift effects.

In lowest order the QED effect on the electron–electron interaction is represented by the diagrams shown in figure 5. The non-radiative part, represented by the diagrams of the first row, have been evaluated for the ground state of He-like ions by Blundell *et al.* [23(a)] and by Lindgren *et al.* [23(b)]. The remaining diagrams represent the radiative part, involving vacuum polarization (second row) and self-energy (third row). This part has been estimated using various approximate schemes, and a full QED calculation has recently been performed by Persson *et al.* [23(c)]. The results are shown in table 1 together with the non-QED parts and compared with the experimental results from the Livermore–GSI collaboration [24]



NVPA and QED results

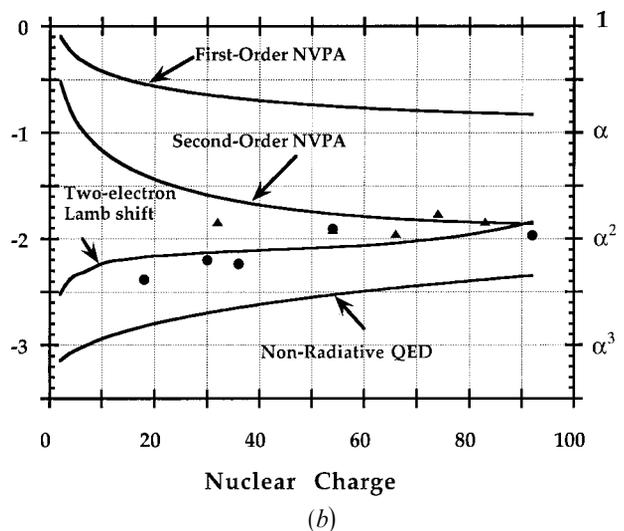


Figure 6. (a) The relative size of the first- and second-order contributions to the two-electron part of the binding energy for He-like ions in the no-virtual-pair approximation (NVPA). The contributions are related to the single-electron binding energy. The scale is logarithmic, one unit corresponding to a factor of $\alpha \approx 1/137$. (b) Same as figure 6(a), where the first- and second-order NVPA contributions are compared with the two-electron Lamb shift and non-radiative QED contributions. Note that for large z the relative first-order contribution is of order α and all second-order effects of order α^2 . Note that the QED effects are of the same order as the second-order NVPA contributions for highly charged ions. The dots represent the uncertainty in the experimental results, X-ray spectroscopy (circular) and electron binding energy (triangular) [33]

In figure 6(a) we have illustrated the first- and second-order non-QED or NVPA (41) contributions to the two-body part of the binding energy for the ground state of

He-like ions. The result is normalized to the single-electron binding energy, and the scale is logarithmic. Obviously, the Coulomb interaction dominates for light elements, but the Breit interaction becomes comparable to the second-order Coulomb interaction already around $Z=20$. The second-order relativistic effects, Coulomb–Breit and Breit–Breit contributions, are quite small for light elements but are of the same order as the second-order Coulomb interaction for heavy ions.

In figure 6(b) the corresponding NVPA and QED results are displayed. The second-order Lamb shift is for medium and highly charged ions comparable to the Coulomb–Breit contribution (see figure 6(a)), while the non-radiative contribution is considerably smaller and comparable with the Breit–Breit interaction. Note that all first-order contributions, including the first-order Lamb shift, for very highly charged ions are of the order of alpha times the one-electron binding energy, while all second-order effects are roughly another factor of alpha smaller.

In figure 6(b) also the uncertainty of the experimental results is indicated. This can be seen to be comparable to the two-electron Lamb shift, which means that this effect is now right on the verge of being detectable.

The experimental uncertainties deduced from X-ray measurements (fine-structure separations) are generally smaller than those deduced from measurements of the binding-energy. In order to compare fine structure results with theory, however, it is necessary to make the evaluations also for excited states. Such calculations have not yet been performed but are now in progress at our laboratory. One problem here is that the two p states, $p_{1/2}$ and $p_{3/2}$, are strongly mixed, and it will be necessary to work with an *extended model space* also for the QED calculations. However, the standard S -matrix procedure is based upon energy conservation (37) and can therefore be employed only for evaluating *diagonal* elements of the effective hamiltonian. Therefore, in order to be able to evaluate also non-diagonal elements, required for an extended model space, some modification of the formalism is required.

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