# Atoms as QED bound atoms

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ABSTRACT. The relevance of Quantum Electrodynamics (QED) in contemporary atomic structure theory is reviewed. Recent experimental advances allow both the production of heavy ions of high charge as well as the measurement of atomic properties with a precision never achieved before. The description of heavy atoms with few electrons via the successive incorporation of one, two, etcetera photons in a rigorous manner and within the bound state Furry representation of QED is technically feasible. For many-electron atoms the many-body (correlation) effects are very important and it is practically impossible to evaluate all the relevant Feynman diagrams to the required accuracy. Thus, it is necessary to develop a theoretical scheme in which the radiative and nonradiative effects are taken into account in an effective way making emphasis in electronic correlation. Preserving gauge invariance, and avoiding both continuum dissolution and variational collapse are basic problems that must be solved when using effective potential methods and finite-basis representations of them. In this context, we shall discuss advances and problems in the description of atoms as QED bound states.

RESUMEN. Se hace una revisión del papel actual de la electrodinámica cuántica (QED) en la teoía de estructura atómica contemporánea. Recientes avances experimentales permitn tanto la producción de iones pesados de alta carga como la medición de propiedades atómicas con una presición sin precedentes. La descripción de átomos pesados con pocos electrones mediante la incorporación sucesiva de efectos de uno, dos, etcetera, fotones en forma rigurosa y en el marco de QED en la representación de Furry es técnicamente factible. Para átomos de muchos electrones los efectos de muchos cuerpos (correlación) son muy importantes y es imposible en la práctica calcular todos los diagrames de Feynman relevantes con la presición requerida. Es entonces necesario generar un esquema en el que los efectos de QED, radiativos y no radiativos, sean incorporados en forma efectiva dando énfasis a la correlción electrónica. La preservación de invariancia de norma, la disolución en el continuo y el colapso variacional son algunos de los problemas que deben resolverse al elegir métodos en que se empleen potenciales efectivos y representaciones matriciales de éstos. En este contexto se describen avances y dificultades en la descripcion de los átomos como estados ligados en QED.

## 1. INTRODUCTION

The development of Quantum Electrodynamics (QED) has been intimately related to the understanding of atomic physics. This can be illustrated by the theoretical advances in the late forties which finally led to a predictive formulation of QED [1]. They were

inspired and motivated by the measurements of one fundamental property of the electron and two atomic properties: the free-electron gyromagnetic factor $g_e$ [2], the Lamb shift [3] and the hyperfine structure in hydrogen [4]. Even nowadays, the excellent agreement between experimental and theoretical evaluations of these quantities constitutes a fundamental test of the validity of QED. However, there are important differences in the difficulties related to the evaluation and measurement of QED effects when going from free electrons into atomic bound electrons. On the one hand, the unprecedented experimental accuracy achieved in the measurement of the free electron $g_e$-factor, $g_e = 2(1 + a_e)$ with $a_e = (1\,159\,652\,188.4 \pm 4.3) \times 10^{-12}$ [5] may be compared with the most accurate rigorous calculation performed within any quantum field theory framework, $a_e = (1\,159\,652\,208 \pm 52) \times 10^{-12}$ [6]. Corrections up to the four photon level were included in this theoretical calculation and its accuracy is at present limited by the uncertainty in the fine structure constant $\alpha$. This constant measures the electron coupling to the electromagnetic field and is the only physical parameter which must unavoidably be introduced in the calculation. On the other hand, for atomic systems there are several relevant physical parameters:

- $\alpha$ which determines the strenght of the interaction between electrons as well as their selfinteraction.

- $Z\alpha$ which conditions likewise the interaction between the electron and the nucleus. It also determines indirectly the velocity of the electrons.

- $N$, the number of electrons in the system.

- $m_e/M_n$, the ratio of the electron and nuclear masses used in the characterization of the center of mass system.

- A, the number of nucleons. It sets the nuclear radius and, in combination with $Z$ it is also relevant for characterizing the strength of the nucleus-electron magnetic and electroweak interactions.

Thus, even though the interactions among the electrons, as well as among the electrons and the nucleus are well "understood", being essentially of electromagnetic nature (corrections due to weak interactions can be incorporated by introducing properly the electroweak nonabelian fields) the complexity of the system necessarily requires reliable approximation schemes to obtain concrete numerical predictions. Such schemes will depend on the values of the physical parameters for each atom.

Lately, there have been experimental advances allowing to observe highly ionized few-electron atoms. For these systems $Z\alpha \approx 1$, so that a nonperturbative treatment in $Z\alpha$ of QED effects is necessary. However, in general, these atoms exhibit small nuclear recoil effects and the interelectron correlation may be evaluated perturbatively. Thus, these atoms are used to test bound interaction picture QED in strong fields.

A more complex problem appears in high-$Z$ many-electron atoms where electron correlation is not negligible and radiative corrections are also important. The accurate characterization of these atoms can be regarded as one of the farthermost limits of theoretical atomic physics.

Finally, for the other atoms, the great experimental advances in the last decade require that electrodynamic relativistic effects have to be taken into account more frequently.

In this work we shall make a brief review of advances achieved by several theoretical groups in the last decade to incorporate QED effects in atomic systems. These effects include both radiative and correlation properties derived from the quantum nature of the electromagnetic and electron fields. The relevance of radiative corrections is particularly important for high-$Z$ few-electron ions. In the next Section, we shall mention some of the experimental techniques presently used. Next, we shall briefly describe the bound-electron QED formalism and how it has been used to obtain numerical predictions for one- and two-electron ions. Then, we shall outline feasible approximation schemes to accurately describe high-$Z$ many-electron atoms. For these systems, the main radiative corrections can be evaluated by similar techniques to those used for few-electron atoms. So that, nowadays, the relativistic correlation problem is considered the bottleneck to be overcome. The kind of problems that have to be solved and the ways used to circumvent them will be described. In particular, the results achieved by our group will be briefly presented in three sections at the end.

## 2. SOME EXPERIMENTAL TECHNIQUES TO OBTAIN HIGH $Z$ FEW-ELECTRON IONS

Highly charged, high-$Z$ ions can be obtained in several ways. Tokamaks and high-power laser- produced plasmas may yield, *e.g.*, nickel-like uranium, $U^{64+}$. At present, higher charge states are studied basically by two techniques:

(a) Beam-foil or beam-gas techniques: After being accelerated at large velocities (velocities comparable to those of the $K$ electron of the projectile to optimize ionization) low-charge ions are sent into light targets where they can be fully stripped. Then the ions go into a thinner "dressing" target where they capture few electrons generally in excited states [7–11]. The photons emitted in flight by the ions are then observed with a detector in the laboratory frame. The Doppler effect limits the accuracy of the data thus obtained mainly due to the uncertainty of the observation angle. The most accurate reported spectroscopic data using this technique correspond to the measurement of the Lambshift of the ground-state of hydrogenlike uranium [11]. It required cooling the ions by electron beams and observing the radiative recombination X-rays at an angle of almost $0^0$.

(b) Electron-beam ion trap: Trapped ions injected in low-charge states or as neutral vapors are ionized to high-charge states by successive collisions with beam electrons [12]. Because collisions with the electron beam results in a heating of the ions, light-ion cooling may be used to prevent detrapping of heavy ions. Notice that electron-beam ion traps use the inverse of the accelerator based beam-foil or beam-gas technique. Instead of a stationary electron target interacting with relativistic ions, the ions in the trap form an almost stationary target interacting with a relativistic electron beam. The accuracy is limited just by the counting statistics [13]. In this way it has been possible to measure, *e.g.*, the two-electron contributions to the ground state of heliumlike Ge, Xe, W, Os and Bi [14], and ionization cross-sections of heliumlike $U^{90+}$ and hydrogenlike $U^{91+}$ [13].

In the near future, these techniques will make it possible to obtain not only more accurate measurements of atomic structure of very highly charged ions, but also to study atomic dynamics in the high-$Z$ regime.

## 3. QED perturbation theory in the bound interaction picture

In the eighties, Mohr proposed [15] to reconsider atomic systems in an unusual way. As a first approximation, the atom would be regarded as a set of non-interacting Dirac electrons and an infinitely heavy nucleus. The main roles of the nucleus would be to provide an *external* potential allowing atom formation and to define a privileged frame of reference for describing the system. Radiative corrections and electron-electron interactions would be regarded as more or less important perturbations produced by interactions of the electrons with the quantized electromagnetic field. The QED perturbation theory built from the basis states of non-interacting Dirac electrons bound in the static field of the nucleus [15, 16] is called bound electron QED. Naturally, these ideas are particularly useful for describing high-$Z$ few-electron ions.

Let us go over the essential features of this formalism. The zero-th order basis states are eigenfunctions of the Dirac equation

$$\hat{h}\psi_n = [-i\hbar c\vec{\alpha}\cdot\nabla + V(\vec{x}) + \beta mc^2]\psi_n(x) = E_n\psi_n(x) \tag{1}$$

for an external potential which in the simplest case is taken as the Coulomb potential generated by a point source

$$V(\vec{x}) = -\frac{Ze^2}{|\vec{x}|}. \tag{2}$$

Under these conditions $\psi_n$ is analitically known both for bound and continuum states and there is a closed expression for $E_n$. When alternative not exactly solvable expressions of the local potential $V(\vec{x})$ are used it is necessary to compute numerically the functions $\psi_n$.[1] The electron-positron field operator $\hat{\Psi}$ is expanded in terms of the annihilation and creation operators,

$$\widehat{\Psi}(x) = \sum \hat{a}_n\psi_n^{(+)}(x) + \sum \hat{b}_n^\dagger\psi_n^{(-)}(x) \tag{3}$$

with the usual anticonmutation rules

$$\{\hat{a}_n, \hat{a}_{n'}^\dagger\} = \delta_{nn'}, \qquad \{\hat{a}_n, \hat{a}_{n'}\} = \{\hat{a}_n^\dagger, \hat{a}_{n'}^\dagger\} = 0, \tag{4}$$

$$\{\hat{b}_n, \hat{b}_{n'}^\dagger\} = \delta_{nn'}, \qquad \{\hat{b}_n, \hat{b}_{n'}\} = \{\hat{b}_n^\dagger, \hat{b}_{n'}^\dagger\} = 0. \tag{5}$$

The electronic vacuum is then defined as

$$\hat{a}_n|0\rangle = \hat{b}_n|0\rangle = 0. \tag{6}$$

The bound-state Green function $S_F$ is given by,

$$S_F(x_2, x_1) = \left\langle 0\left|\hat{T}\left[\widehat{\Psi}(x_2)\widehat{\overline{\Psi}}(x_1)\right]\right|0\right\rangle \tag{7}$$

$$= \frac{1}{2\pi i}\int_{-\infty}^{\infty} dz \sum_n \frac{\psi_n(\vec{x}_2)\overline{\psi}_n(\vec{x}_1)}{E_n - z(1 + i\delta)} \tag{8}$$

with $\hat{T}$ the time-ordering operator.

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[1]In fact, at present, numerical codes are written in such a way that even in the case of knowning $\{\psi_n\}$ analytically it is more convinient to work with its numerical representations.

In an analogous way, one starts from the quantized free electromagnetic field:

$$\hat{A}_\mu = \sum_{k\lambda} \mathbf{e}_\mu^\lambda [\hat{c}_{k\lambda} N_k e^{ik_\nu x^\nu} + \hat{c}_{k\lambda}^\dagger N_k e^{-ik_\nu x^\nu}]. \tag{9}$$

Here $\mathbf{e}_\mu^\lambda$ denotes the unitary polarization vectors and $N_k$ the normalization factor of the $k_\nu$ electromagnetic mode. The usual commutation relations are imposed on the operators $\hat{c}_{k\lambda}$, that is

$$\{\hat{c}_{k\lambda}, \hat{c}_{k'\lambda'}^\dagger\} = \delta_{kk'}\delta_{\lambda\lambda'}, \qquad \{\hat{c}_{k\lambda}, \hat{c}_{k'\lambda'}\} = \{\hat{c}_{k\lambda}^\dagger, \hat{c}_{k'\lambda'}^\dagger\} = 0. \tag{10}$$

The free electromagnetic vacuum is defined as

$$\hat{c}_{k\lambda}|0\rangle_{\mathrm{EM}} = 0. \tag{11}$$

Thus, the Feynman gauge photon propagator $D_F$ is given by

$$g_{\mu\nu} D_F(x_2, x_1) = {}_{\mathrm{EM}}\Big\langle 0 \Big| \hat{T}\Big[\hat{A}_\mu(x_2)\hat{A}_\nu(x_1)\Big] \Big| 0 \Big\rangle_{\mathrm{EM}} \tag{12}$$

$$= -g_{\mu\nu}\frac{4\pi i}{(2\pi)^4} \int d^4k \frac{e^{-ik(x_2-x_1)}}{k^2 + i\delta}. \tag{13}$$

As usual, the noninteracting field Hamiltonian density $\widehat{H}_0$ is defined by the normal ordered operator

$$\widehat{H}_0 = \widehat{H}_0^e + \widehat{H}_0^{\mathrm{EM}} \tag{14}$$

$$\widehat{H}_0^e = \,: \widehat{\Psi}^\dagger(x)\hat{h}\widehat{\Psi}(x) : \tag{15}$$

$$\widehat{H}_0^{\mathrm{EM}} = \frac{1}{16\pi} : \widehat{F}_{\mu\nu}(x)\widehat{F}^{\mu\nu}(x) : \tag{16}$$

while the Hamiltonian density for the interaction between the electron-positron field and the radiation field is

$$H_I(x) =: \hat{j}_\mu(x)\hat{A}^\mu(x) : \tag{17}$$

with $j_\mu = e\widehat{\overline{\Psi}}(x)\gamma_\mu\widehat{\Psi}(x)$ the electron-positron current. In the bound state interaction picture the state vector wavefunction evolves according to

$$i\hbar\frac{\partial}{\partial t}|\Phi(t)\rangle = \widehat{H}_{\mathrm{INT}}|\Phi(t)\rangle \qquad \widehat{H}_{\mathrm{INT}} = e^{i\widehat{H}_0 t}\widehat{H}_I e^{-i\widehat{H}_0 t}, \tag{18}$$

whereas any operator $\widehat{F}$ evolves according to the equation

$$-i\hbar\frac{\partial}{\partial t}\widehat{F} = \Big[\widehat{H}_0, \widehat{F}(t)\Big]. \tag{19}$$

The evolution operator $\widehat{U}(t, t_0)$ satisfies the equation

$$-i\hbar\frac{\partial}{\partial t}\widehat{U}(t, t_0) = \widehat{H}_{\mathrm{INT}}\widehat{U}(t, t_0). \tag{20}$$

Now, one of the purposes of bound electron QED is the calculation of the energy shifts due to the interelectronic interaction. This interaction is present all the time. Thus, in order to apply the usual scattering techniques of standard QED, Gell-Mann and Low [17] introduced the adiabatic Hamiltonian

$$\widehat{H}_{\text{INT}}(t,\gamma) = e^{-\gamma(t)}\widehat{H}_{\text{INT}}(t) \qquad \lim_{t \to \pm\infty} \gamma(t) = 0. \tag{21}$$

Usual QED is applied and at the end of the calculations the limit $\gamma \to 0$ is taken. The energy shift due to the interaction of a state $|\Psi_a^0\rangle$ with the quantized field is then given by the Gell-Mann and Low expression

$$\Delta E_a = \lim_{\gamma \to 0} ie\,\gamma \frac{(\partial/\partial e)\langle\Psi_a^0|\widehat{U}_\gamma(0,-\infty)|\Psi_a^0\rangle}{\langle\Psi_a^0|\widehat{U}_\gamma(0,-\infty)|\Psi_a^0\rangle} \tag{22}$$

or in terms of the scattering operator $S_\gamma = \hat{U}_\gamma(\infty,-\infty)$ [18]

$$\Delta E_a = \frac{1}{2}\lim_{\gamma \to 0} ie\,\gamma \frac{(\partial/\partial e)\langle\Psi_a^0|\widehat{S}_\gamma|\Psi_a^0\rangle}{\langle\Psi_a^0|\hat{S}_\gamma|\Psi_a^0\rangle}. \tag{23}$$

The perturbative expansion for the adiabatic scattering operator is as usual

$$\hat{S}_\gamma = 1 + \sum_{j=1}^{\infty} \hat{S}_\gamma^{(j)} \tag{24}$$

with

$$\hat{S}^{(j)} = \frac{-i^j}{j!} \int d^4x_1 \int d^4x_2 \ldots \int d^4x_j \widehat{T}[H_{\text{INT}}(\gamma,x_1)H_{\text{INT}}(\gamma,x_2)\ldots H_{\text{INT}}(\gamma,x_j)]. \tag{25}$$

For the free atom, in the absence of external fields, the energy corrections contain only $S$-matrix elements of even order. The reason is that the perturbation $\widehat{H}_{INT}$ contains the operators of the emission or the absorption of the photon and they should enter pairwise in the final expression to give the photon vacuum state. The electron-positron state $|\Psi_a^0(x)\rangle$ is usually taken as an eigenstate of the bound state fermionic number operator, the parity operator, the total angular momentum and its $z$ component.

## 4. APPLICATION OF BOUND STATE FORMALISM TO ONE-ELECTRON IONS.

For this case, the first order and second order Feynman diagrams in $\alpha$ are drawn in Fig. 1. The first order diagrams are: (a) the self-energy (SE), and (b) the vacuum polarization (VP) diagrams.

In order to isolate the divergences that arise in the calculation [19–22], the bound state propagator can be expanded into a free-electron propagator, a first-order Coulomb scattered term and higher order scattered terms. The higher order part can be written in a compact form using a combination of free- and bound-electron propagators. The terms that result divergent consist of combinations of free-electron propagators and photon
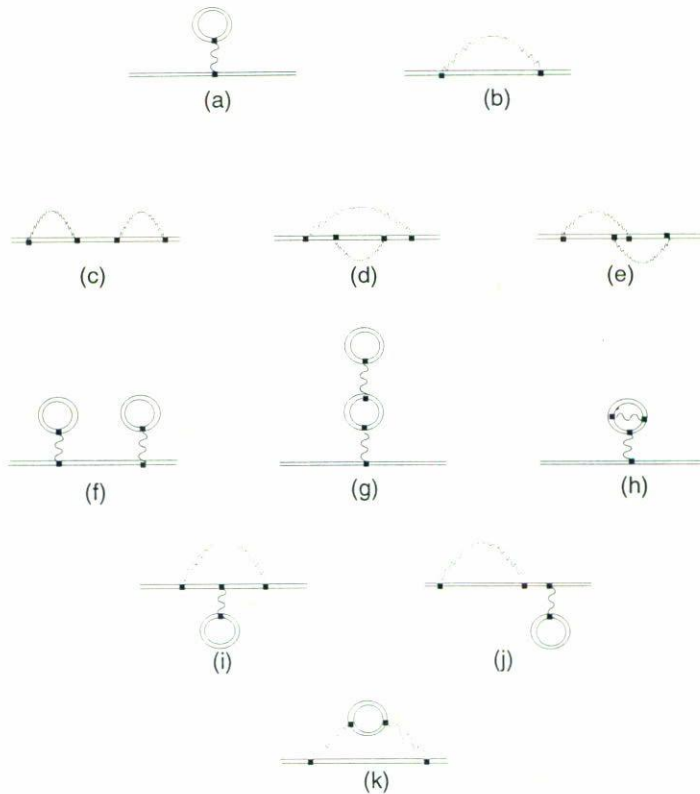
FIGURE 1. One-photon and two-photon Feynman diagrams for one-electron atoms in the bound formalism of QED. The one-photon diagrams are (a) the self-energy (SE), and (b) the vacuum polarization (VP) diagrams. The two-photon diagrams are: self-energy-self-energy (SESE) [diagrams (c)–(e)], vacuum polarization-vacuum polarization (VPVP) [diagrams (f)–(h)], self-energy-vacuum polarization (SEVP) [diagrams (i)–(j)], and self-vacuum-polarization-energy [S(VP)E] [diagram (k)].

propagators which can be treated analytically so that the divergences are isolated and substracted using standard QED techniques. In fact the many-potential part of the SE diagram is free from divergences allowing its direct evaluation using techniques such as numerical basis-set approaches. This has made it possible to include realistic nuclear charge distributions such as two-parameter Fermi and deformed Fermi model distributions in the calculation. An alternative to evaluate the SE correction was recently proposed [23, 24]. It consists in decomposing both the unrenormalized bound-state SE and mass term into divergent sums over finite partial-wave contributions. The renormalization substraction is then performed at the partial-wave level and a convergent renormalized bound-state SE is obtained.

The VP correction is usually divided into a dominating Uehling part [25, 26] and a Wichmann-Kroll part [27]. The Uehling term gives an effective correction to the nucleus potential which can be computed in a straighfoward way. The Uehling potential in

coordinate space is

$$\mathcal{V}_U = -\frac{e^4 Z}{3\pi} \int_0^\infty d\Xi \left(2 + \frac{1}{\Xi^2}\right) \frac{\sqrt{\Xi^2 - 1}}{\Xi^2} \int d^3 x\, \rho(\vec{x}) \frac{\exp(-2mr\Xi|\vec{r} - \vec{x}|)}{|\vec{r} - \vec{x}|}, \qquad (26)$$

with $\rho(\vec{x})$ the nuclear charge density. Explicit evaluations of its contribution to the energy correction can be found in Ref. 28. The Wichmann-Kroll correction evaluated to all orders in $Z\alpha$ by Soff and Mohr [29] gives a correction to the energy of the form

$$\Delta E_{WK} = \frac{\alpha}{\pi} \frac{(\alpha Z)^4}{n^3} H(\alpha Z). \qquad (27)$$

State dependent values of the function $H(\alpha Z)$ are tabulated in Ref. 29 using a spherical shell distribution for the nucleus.

The two-photon QED effects [30] are classified as self-energy-self-energy (SESE) [diagrams (c)–(e) of Fig. 1], vacuum polarization-vacuum polarization (VPVP) [diagrams (f)–(h) of Fig. 1], self-energy-vacuum polarization (SEVP) [diagrams (i)–(j) of Fig. 1] and self-vacuum-polarization-energy [S(VP)E] [diagram (k) of Fig. 1]. These corrections represent separately gauge invariant sets. Almost all of them have been recently evaluated for H-like uranium which has become the standard test case of QED in one-electron ions. For this ion, the VPVP diagram (f) has been evaluated by Persson *et al.* [31, 32] and the VPVP diagrams (g,h) known as Källén- Sabry contributions were computed by Beier and Soff [33] and by Schneider *et al.* [34] in the Uehling approximation. The SEVP corrections can be found in Ref. 31 while the S(VP)E correction in the Uehling approximation has been reported in Ref. 32. The SESE diagram (c) has been evaluated at the irreducible part level [35]. It is gauge dependent. The value of the remaining part of (c) and diagrams (d) and (e) have not yet been reported in the literature. This is due to problems in the renormalization structure of SESE contributions.

Before performing a comparison with experimental values it is necessary to evaluate nuclear recoil and polarization effects not taken into account in the bound-state QED formalism. Nuclear recoil can be studied within the Salpeter formalism [36] and for H-like uranium this has been done by Artemyev *et al.* [37]. The nuclear polarization effects arise from the interactions between the electron and excited states of the nucleus [38].

By convention, all corrections beyond the point nucleus Dirac eigenvalue except the non-relativistic reduced mass correction given by $[m/(m + M)]E_n$ and the contributions due to hyperfine structure are called Lamb shift correction. Taking into account all effects described in this section, the theoretical Lamb shift of H-like uranium gives [30] the value 465.5±2 eV with the main uncertainty arising from the SESE diagrams that have not been calculated yet. The latest reported experimental value [11] is $470 \pm 16$ eV. Substantial experimental advances have been achieved lately so that important improvements in the accuracy are expected.

## 5. TWO-ELECTRON HIGH-$Z$ IONS.

The Feynman diagrams for the first-order expansion consist of the one-exchanged photon correction, SE and VP. They are shown in Fig. 2. Within this formalism, the SE and VP for the two electron atom are just equal to the corresponding one-particle corrections.

(a)                                    (b)                                    (c)
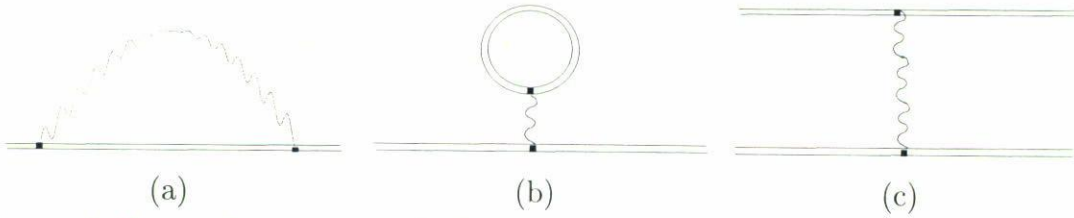
FIGURE 2. For two-electron atoms, the Feynman diagrams for the first-order perturbative expansion in the bound formalism of QED are: (a) the one-exchanged photon diagram, (b) the SE diagram and (c) the VP diagram.

The one-exchanged-photon correction to the energy can be written [15] as a direct term which is real:

$$E_d = e^2 \int d^3x_2 \int d^3x_1 \, \Psi^\dagger(\vec{x}_2, \vec{x}_1) \frac{1}{|\vec{x}_2 - \vec{x}_1|} \alpha_\mu^{(2)} \alpha^{\mu(1)} \Psi(\vec{x}_2, \vec{x}_1), \tag{28}$$

and an exchange term which is complex:

$$E_e = e^2 \int d^3x_2 \int d^3x_1 \, \Psi^\dagger(\vec{x}_2, \vec{x}_1) \frac{e^{i|\eta||\vec{x}_2 - \vec{x}_1|}}{|\vec{x}_2 - \vec{x}_1|} \alpha_\mu^{(2)} \alpha^{\mu(1)} \Psi(\vec{x}_1, \vec{x}_2), \tag{29}$$

with

$$\eta = [E_{\beta2} - E_{\beta1}]/\hbar. \tag{30}$$

The imaginary part of the exchange term corresponds to a partial width contribution to the excited-state resonance associated to the decay to the ground state. The reminder of the natural width arises from the imaginary part of the self energy. The real part of the sum of the direct and exchange term gives the Feynman gauge form of the one-exchanged photon correction. By direct calculation [39], it can be shown to be equal to the Coulomb gauge expression which consists of a static Coulomb interaction:

$$\frac{e^2}{|\vec{x}_2 - \vec{x}_1|}; \tag{31}$$

and the Breit interaction

$$-\frac{e^2}{2} \left\{ \frac{\vec{\alpha}_1 \cdot \vec{\alpha}_2}{|\vec{x}_2 - \vec{x}_1|} + \frac{[\vec{\alpha}_1 \cdot (\vec{x}_2 - \vec{x}_1)][\vec{\alpha}_2 \cdot (\vec{x}_2 - \vec{x}_1)]}{|\vec{x}_2 - \vec{x}_1|^3} \right\} \tag{32}$$

when time retardation is neglected ($\eta = 0$).

The two-photon contributions to the electron-electron interaction of two-electron atoms are shown in Fig. 3. The non-radiative correlation part corresponds to the ladder, (a) in Fig. 3, and crossed-photon diagrams, (b) in Fig. 3. They have been directly evaluated for the ground state of He-like ions by Lindgren et al. [40] in both Feynman and Coulomb gauge verifying gauge invariance to numerical accuracy. The two-electron
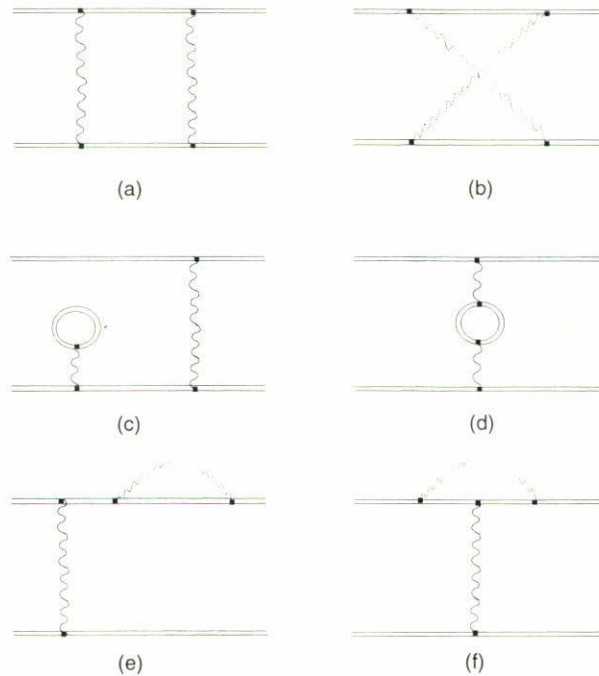
FIGURE 3. The two-photon contributions to the electron-electron interaction of two-electron atoms are: the correlations diagrams (a) ladder, and (b) crossed-photon; the two-electron Lamb shift diagrams of VP, diagrams (c) and (d), and of SE, diagrams (e) and (f).

Lamb shift, *i.e.*, vacuum polarization, (c) and (d) in Fig. 3, and self energy, (e) and (f) in Fig. 3, have been directly calculated by Persson *et al.* [41] using a finite nucleus and a uniform charge distribution. To a first approximation, (e) and (f) can be regarded as a *screening* of the single-electron Lamb shift which can be estimated by modifying the nuclear potential [23, 42, 43].

Experimentally, the ionization energy of heliumlike ions has been compared with that of hydrogenlike ions. This has allowed to measure the two-electron contributions to the ground state of He-like ions. However, the estimated theoretical uncertainty is $\pm 0.1$ eV [41], much lower than the reported experimental one which ranges from $\pm 1.6$ eV for Ge ($Z = 32$) to $\pm 14$ eV for Bi [14].

## 6. MANY-ELECTRON ATOMS.

When dealing with more than two-electron atoms it becomes very complicated to treat the system by evaluating one, two, ... , etc. photon diagrams in a successive way. At least two alternatives have been explored.

The first one [44–46] corresponds to using effective one-particle local potentials $U_{\text{eff}}$ in terms of which the Furry representation is worked out. These model potentials try to take approximately into account the interaction between electrons in atoms. In the simplest cases they are taken as central potentials inferred from Hartree-Fock calculations. The

S-matrix approach described in Sect. 3, is constructed and three different type of diagrams can be considered. The first class corresponds to photon exchange diagrams which may be connected with many-body perturbation theory (MBPT) diagrams. The second corresponds to pure radiative correction diagrams and the third to radiative-correlation diagrams. This classification of diagrams has already been illustrated for two electron atoms in Fig. 3. The difference is that the electron legs and electron Green functions considered here include the effects of the effective local potential $U_{\mathrm{eff}}$. In general, radiative QED corrections are dominated by the one-electron Lamb shift [45]. These SE and VP corrections are evaluated using the techniques mentioned in Sect. 4 for hydrogenic ions but considering the screening effect contained in $U_{\mathrm{eff}}(r)$ [46]. Thus, the third class of radiative-correlation diagrams is expected to give a small contribution whenever the local potential $U_{\mathrm{eff}}(r)$ gives a good zeroth-order approximation to the electron-electron interaction. In principle the problem is basically reduced to evaluate the correlation diagrams via MBPT. However, as we shall see below, besides possible convergence problems, relativistic many-body perturbation theory (RMBPT) has peculiarities of its own requiring more than a simple extension of its nonrelativistic counterpart.

A second alternative is to define an $N$-electron Hamiltonian [40, 47],

$$H = \sum_{n=1}^{N} h_D(n) + \sum_{m<n}^{N} V_{mn} + \sum_{m<n<p}^{N} V_{mnp} + \dots . \tag{33}$$

Here $h_D$ is the single-electron Dirac Hamiltonian and $V_{mn}, V_{mnp}, \dots$, are effective two-, three-, etc., electron potentials defined by means of QED in the bound state picture which starts solely from the electron-nucleus interaction. Radiative effects are treated separately and the radiative-correlation diagrams, sometimes called screened Lamb-shift diagrams, must be taken into account in an accurate treatment. Actual calculations in general use just two-body potentials $V_{mn}$. Explicit expressions for three-body potentials have been obtained by Mittleman [48] using a formalism originally suggested by Schwinger [49]. This method decouples, via a unitary transformation, virtual photons in the radiation field from the matter field. The contribution of the three-body potential to the binding energy of a lithiumlike atom was found to be less than 0.021 eV [50].

In the scheme of work we are describing, it is necessary to establish a clear relationship between the effective potentials $V_{m_i m_j \dots m_k}$, the degree of accuracy of the $N$-particle wavefunctions obtained using approximate schemes to solve Schrödinger-like equations related to $H$, and the Feynman diagrams of QED. This point can be illustrated by studies on gauge invariance within the Dirac-Hartree-Fock (DHF) formalism using single photon potentials derived from QED. These studies show that potentials obtained in Feynman and Coulomb gauges [51] lead to different numerical results in self-consistent field (SCF) DHF calculations. As shown by Lindgren [52], this is a consequence of the fact that SCF as well as any other method based on iterative use of single-photon potentials yields only a part of the higher-order diagrams. In second-order, the crossed-photon diagram and a part of the uncrossed-photon diagram are omitted. These effects have been shown to be significantly larger in the Feynman gauge than in the Coulomb gauge. Thus even though the results of QED are gauge independent in each order of perturbation theory, the results obtained from effective potentials may be gauge dependent with this dependence

conditioned by the method of solving the $N$-particle problem. Another example of this problem corresponds to the use of the time-retarded Breit interaction, mentioned in Section 5, beyond first order MBPT. Such a procedure is not meaningful unless virtual-pair effects are considered also [40].

## 7. THE RELATIVISTIC MANY-BODY PROBLEM.

Once a relativistic many-body Hamiltonian has been obtained as an *ever* approximate representation of the atom, it is necessary to find a numerical scheme to work it out. In the beginning, it was expected that a direct generalization of the approximation methods of the nonrelativistic many-body problem could be used. Usual nonrelativistic *ab initio* methods are essentially of two types:

- The Hartree-Fock approximation obtained via either a numerical solution or a basis set approximation.
- Beyond Hartree-Fock via either a perturbative approach or a variational approach, the latter supported by a variational theorem.

In the late sixties and across the seventies, great efforts were devoted to the solution of the Hartree-Fock equations which result from considering the Hamiltonian of the form (34) with a two-body potential containing the Coulomb interaction,

$$H_C = \sum_{n=1}^{N} h_D(n) + \sum_{m<n}^{N} \frac{e^2}{r_{mn}}, \tag{34}$$

and, sometimes, unretarded Breit interaction,

$$H_{CB} = \sum_{n=1}^{N} h_D(n) + \sum_{m<n}^{N} \frac{e^2}{r_{mn}} - \frac{e^2}{2} \left[ \frac{\vec{\alpha}_m \cdot \vec{\alpha}_n}{r_{mn}} + \frac{(\vec{\alpha}_m \cdot \vec{r}_{mn})(\vec{\alpha}_2 \cdot \vec{r}_{mn})}{r_{mn}^3} \right]. \tag{35}$$

Computer algorithms for obtaining numerical finite-difference solutions were implemented by Grant [53] and Desclaux [54]. Although for some atomic systems serious problems of convergence could arise, these approaches led to the first DHF results. An alternative to this numerical approach is to search for analytical approximations to DHF solutions. Kim [55] pioneered the DHF self-consistent-field method using finite-basis representations of the approximate wavefunctions. His work revealed a tendency for calculated energies to *fall* below the variational limit. This effect is known as *variational collapse* [56] and has been found in variational approaches of simpler systems such as hydrogenic ones. That is, *a naive variational calculation using a Dirac-like Hamiltonian may cause the predicted eigenvalues to sink towards minus infinity.* This phenomena is not surprising due to the fact that, in general, Dirac Hamiltonians admit a continuum of negative-energy eigenstates so that their spectra are not bounded from below. Thus, the applicability of the usual quantum mechanical variational theorem is not direct. However, variational collapse also arises because finite-basis representations of Dirac-like Hamiltonians do not always reproduce essential qualities of the original operator. In order to illustrate this point, let us remember that the eigenvalue equation for even a one-particle Dirac

Hamiltonian $h_D$ is a system of coupled equations for the so called "small" and "large" components. Thus, in order to be reliable, a finite-basis representation of $h_D$ must allow the possibility of approximately representing such a coupling [57, 58].

Now, the implementation of nonrelativistic many-body perturbation techniques to Dirac Hamiltonians is not straightfoward either. As first reported by Brown and Ravenhall [59], a conventional perturbative calculation should start from a complete set of eigenfunctions of a zeroth-order Dirac Hamiltonian $H_0$. This complete set includes negative-energy states. Second- and higher-order perturbative corrections would make such states to appear as virtual electron-positron pairs which, however, are not experimentally observed. Mathematically, it is not possible to apply naively standard perturbation theory because the spectrum of a system of $N$ noninteracting electrons will exhibit an infinite order degeneracy due to the presence of the negative energy continuum in the spectrum of each individual electron. This effect is known as *continuum dissolution*. Brown and Ravenhall conclude from this that the use of an $N$-particle Hamiltonian is meaningless since starting from a noninteracting $N$-electron Hamiltonian "by turning on slowly the electron-electron interaction the system can make real transitions to states where one electron has a large negative energy and the other electron is in the positive-energy continuum."

In order to give a computational scheme which allowed the use of MBPT techniques an approach known as *no-(virtual)-pair approximation* was proposed [60]. It consists in replacing the $N$-particle model Hamiltonian $H_D$ by its projected counterpart

$$H_D^{NP} = \Lambda_+ H_D \Lambda_+. \tag{36}$$

where $\Lambda_+$ is the projection operator constructed as the product of one-particle positive energy projection operators determined by a one particle Hamiltonian $h_0$. The use of such projection operators was formally proposed by Brown and Ravenhall who in fact chose $h_0$ as the free-particle Dirac-Hamiltonian. Later Sucher [62] advocated the use of such projectors, however numerical results on the hydrogen atom [63] led to very bad estimates of the spectra showing its inapplicability. Thus, $H_D^{NP}$ is highly dependent on the one-particle Hamiltonian $h_0$ used to define $\Lambda_+$ [61]. The important point is that the definition of one-particle positive states depends on the Hamiltonian.[2]

Adequate projection operators, $\Lambda_+$, discriminating between $(+)$ and $(-)$ states were proposed by a number of authors [45, 61, 65]. In particular, the $\Lambda_+$ which makes the energy stationary when the wave function is a single determinant turns out to be precisely the projection into DHF orbitals [65]. When working with a Hamiltonian with the structure of Eq. (34) with two-body interactions, taking the one-particle Hamiltonian $h_0$ as $h_D$ guarantees that the no-pair *approximation* is correct to order $O(\alpha^2)$ [60]. However, even with this choice, attempts to obtain explicit expressions for $\Lambda^+$ have been sterile [66]. Meanwhile, people have resorted to *very large* basis sets from which a partition into $(+)$ and $(-)$ states is made. A most successful scheme to construct $(+)$ one-particle states

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[2]In other areas of physics such as quantum theory in the presence of gravitational fields or quantum optics the dependence of the positive- and negative-states definition on the wave-equation has been lately exploited. In particular the Bogolubov formalism permits to quantify the mixing of positive- and negative-states for different wave-equations with equal boundary conditions [64].

was proposed by Johnson *et al.* [67] whereby $h_0 = h_D$ is placed in a cavity of radius $R \approx 40$ a.u., *viz.*, surrounded by an infinite potential barrier at $r = R$; also, each large component is required to be equal to its partner small component at $r = R$ in order to avoid Klein's paradox. The basis sets are B-splines [68]. Using MBPT based on the projected Hamiltonian $H_D^{NP}$ constructed in this way has led to quite precise estimates for the lowest energies of some many-electron ions [45, 69–71].

For systems where high-order MBPT contributions are not negligible, *e.g.* most neutral atoms, alternative schemes must be used to take into account correlation in an accurate way. Among them there is the coupled cluster (CC) approach which leads to all-order equations that upon iteration yield order-by-order expressions for the Rayleigh-Schrödinger linked-diagram expansion [72]. Its reliable implementation for relativistic many-body systems is a challenging problem to which several groups are devoted and some applications have appeared lately [73].

Two other promising alternatives are the configuration interaction (CI) [76–81] and the multiconfigurational Dirac-Hartree-Fock (MCDF) [74, 75] approaches. They are variational techniques which go beyond the independent particle model. Lacking a variational theorem that can be directly applied to the $N$-particle Dirac equation, the reliability of these approaches is not clear in general. In fact, whether the use of projection operators is necessary or not in the MCDF case has been controversial [74]. In the next section, we shall present a version of the variational theorem which, within the CI scheme, overcomes variational collapse and continuum dissolution, and yields upper bounds to the energies obtained with projection operators independently of the one-particle Hamiltonian used to define them [81].

## 8. A variational theorem for relativistic configuration interaction.

One of the most useful tools in *ab initio* electronic structure calculations is configuration interaction. It is a variational method which replaces the time independent Schrödinger equation with a finite matrix eigenvalue equation:

$$H\Phi_i = E\Phi_i \rightarrow \mathbf{H}\mathbf{C}_i = E\mathbf{C}_i \tag{37}$$

via the approximation

$$\Phi_i \quad \rightarrow \quad \sum_{Kg} C_{iK}^{(g)} \phi_K^{(g)}, \tag{38}$$

$$H \quad \rightarrow \quad \rangle\phi_K^{(g)}|H|\phi_{K'}^{(g')}\rangle. \tag{39}$$

The configuration-state-functions $\phi_K^{(g)}$ are linear combinations of Slater determinants $D_{K\alpha}$ associated to the configuration K . They are built so that each $\phi_K^{(g)}$ is an eigenvector of the recognized symmetries of the Hamiltonian, thus

$$\phi_K^{(g)} = \sum_{\alpha=1}^{n_K} D_{K\alpha}\, c_{\alpha g}, \tag{40}$$

where $g$ is a degenerancy index to distinguish configuration state-functions with the same eigenvalues of the symmetry operators.

Here we shall consider an $N$-particle Dirac-like Hamiltonian,

$$H = \sum_{i=1}^{N} h_D(i) + V_{e-e}, \tag{41}$$

$$h_D = c\vec{\alpha} \cdot \vec{p} + \beta mc^2 + V_N \tag{42}$$

where $V_N$ represents a central-nuclear potential and $V_{e-e}$ denotes the interaction between the electrons. Thus, the configuration-state-functions are eigenfunctions of the total angular momentum operators $J^2$ and $J_z$ as well as the parity operator $P$. The Slater determinants $D_{K\alpha}$ are formed from a one-particle basis set of bispinors $\Psi_{n_i l j m_j}$. The "large" and "small" components must be continuously differentiable on $r$ in $(0, \infty)$. For bound states, they decay at least exponentially for $r \to \infty$. They must also satisfy the correct boundary conditions imposed by the nuclear potential $V_N$.

A variational theorem for relativistic CI can be formulated as follows [82]:

Let us consider a one-particle basis set $B_m^{(1)}$ of dimension $m$ of orthonormalized spherical Dirac bispinors $\Psi_{n_i l j m_j}$. With the one-particle basis $B_m^{(1)}$ we can construct a finite-basis representation $\mathbf{h}_0$ of any one-particle Hamiltonian $h_0$ including $h_D$. We shall assume that $\mathbf{H}_0$ is hermitean.

Let $B_{K_m}^{(N)}$ be the $N$-particle basis set of dimension $K_m$ constituted by *all* possible configuration-state-functions $\Psi_i$ that can be constructed from $B_m^{(1)}$ and are eigenfunctions of all known symmetry operators associated to $H$. With this basis a finite-basis representation $\mathbf{H}^{\mathcal{B}}$ of the $N$-particle Hamiltonian $H$ is uniquely determined by the one-particle basis set. If $\mathbf{H}^{\mathcal{B}}$ is hermitean then the eigenvalue equation

$$\mathbf{H}^{\mathcal{B}} \mathbf{C}_i^{\mathcal{B}} = E_i^{\mathcal{B}} \mathbf{C}_i^{\mathcal{B}} \tag{43}$$

can be solved. The eigenvalues $E_i^{\mathcal{B}}$ are arranged in nondecreasing order:

$$E_1^{\mathcal{B}} \leq E_2^{\mathcal{B}} \cdots \leq E_{N_m}^{\mathcal{B}}. \tag{44}$$

A similar equation can be written for $\mathbf{h}_0$. The corresponding one-particle eigenfunctions can be classified according to the sign of the eigenvalue $\epsilon_i$. If there exist eigenvalues of $\mathbf{h}_0$ greater than zero, a one-particle basis set of dimension $0 < m_{h_0}^+ \leq m$ can be formed just by the one-particle eigenfunctions with positive eigenvalues. We can consider the corresponding full $N$-particle basis set $\mathcal{B}_{K_{m+}}^{(N)}$ and the corresponding finite-basis representation of $H$. According to usual terminology the latter will be denoted by $\mathbf{H}_{h_0}^{(NP)\mathcal{B}}$, NP meaning no-pair, with a similar notation for the eigenvalues $E_{h_0}^{(NP)\mathcal{B}}$.

Let us recall the bracketing theorem [83], known since 1847. It asserts that given a hermitean matrix representation of an operator $W$ in a given orthonormal basis of dimension $m$ with eigenvalues $W_{m,1} \leq W_{m,2} \cdots \leq W_{m,m}$, upon increasing the basis by an

extra orthonormal function the positions of the $m+1$-th relative to the $m$-th eigenvalues fulfill

$$W_{m+1,1} \leq W_{m,1} \leq W_{m+1,2} \cdots \leq W_{m+1,m} \leq W_{m,m} \leq W_{m+1,m+1}. \tag{45}$$

This theorem is the theoretical basis for obtaining nonrelativistic approximate eigenvalues for excited states using the Rayleigh-Ritz variation method, of which configuration interaction is an example.

As a corollary of this theorem, if $m_{h_0}^+$ is strictly less than $m$ it follows that

$$E_i^{(NP)\mathcal{B}} \leq E_{K_m - K_{m^+} + i}^{\mathcal{B}} \qquad i = 1, \ldots, K(m_{h_0}^+). \tag{46}$$

In short, independently of the selection of the one-particle Hamiltonian $h_0$, strict *upper* bounds to the *no-pair* eigenvalues can be obtained by considering the correct eigenvalue of the matrix $\mathbf{H}^{\mathcal{B}}$.

## 9. ONE-PARTICLE BASIS SETS.

As mentioned in the last section, obtaining reliable finite-basis representations $\mathbf{h}_0$ of a one-particle Dirac Hamiltonian $h_0$ is not a trivial task. The spectra related to the matrix $\mathbf{h}_0$ may exhibit spurious unphysical solutions, an extreme sensitivity to the details of the basis and may yield positive energies much lower than the exact energies. In general, accurate representations of positive energy bound states require the basis to satisfy correct boundary conditions and to yield the correct non-relativistic limit.

Let us consider a basis set of dimension $2m$ that permits to write the radial part of the one-particle upper and lower components as linear combinations of $m$ given $P_{il\kappa}(r)$ and $mQ_{il\kappa}(r)$ functions. If these $2m$ functions are properly selected the spectrum of $\mathbf{h}_0$ will contain just $m$ positive energies which, under variational optimization of the parameters in the basis, approximately represent the $m$ lowest positive eigenvalues of the one-particle Hamiltonian $h_0$. The other $m$ negative energies and eigenvalues are usually ignored. For obtaining this controlled partitioning, it has proven necessary that the $\{P_{il\kappa}(r)\}$ set be functionally related to the $\{Q_{il\kappa}(r)\}$ set by pairs. In our case, we find convenient to write this $2m$ dimensional basis as an $m$-dimensional one-particle basis of normalizable Dirac bispinors embracing $n_{irr}$ irreducible representations:

$$\Psi_{n_i l j m_j}^{(i)} = \frac{1}{r} \begin{pmatrix} P_{n_i l j}(r) \mathcal{Y}_{\kappa m_j} \\ i Q_{n_i l' j}(r) \mathcal{Y}_{-\kappa m_j} \end{pmatrix}, \qquad i = 1, 2, \ldots, i_x(lj), \tag{47}$$

$$m = \sum_{(lj)=1}^{n_{irr}} i_x(lj). \tag{48}$$

supplemented with another complementary set of $m$ *Dirac* bispinors,

$$\Psi_{n_i l j m_j}^{(i+m)} = \frac{1}{r} \begin{pmatrix} P_{n_i l j}(r) \mathcal{Y}_{\kappa m_j} \\ -i Q_{n_i l' j}(r) \mathcal{Y}_{-\kappa m_j} \end{pmatrix}, \tag{49}$$

differing from the first $m$ in the minus sign preceding the lower components $Q$. We shall call the first one-particle basis a single primitive (SP) set and the full $2m$-dimensional basis a double-primitive (DP) set. This kind of basis has been used for hydrogenic Hamiltonians $h_D$ for states with $\kappa < 0$ [84] and, with one exception [85, 86], in *all* finite-basis DHF calculations [87–89].

In fact, there are several useful selections of $\{P_{ilj}\}$ and $\{Q_{ilj}\}$ that have been introduced in the literature. Some of these sets require that certain parameters characterizing them are equal for several radial functions but are otherwise unrestricted. Other basis sets are useful just in a restricted range of values of its parameters. A review of the actual behavior of several basis sets for $Z \leq 118$ and a wide range of the nonlinear parameters involved is given in Ref. 90.

Notice that a DP set is invariant under *separate* nonsingular linear transformations of its upper and lower components. Also, in connection with having an equal number of positive- and negative-energy one-particle functions, it may be noticed that the trace of the kinetic energy operator $c\vec{\alpha} \cdot \vec{p}$ for any DP set is identically zero, irrespective of the values of the nonlinear parameters used to define $P$ and $Q$, and of $lj$ quantum numbers.

## 10. Relativistic CI and projection operators.

We will now focus on configuration interaction (CI) expansions in which *all* configuration state functions that can be constructed from the given one-particle basis are included, known as *full* CI. Full CI is always an absolute invariant, *viz.*, the spectrum is independent of linear transformations within the one-particle basis set.

Let us now consider a full CI expansion using the entire $2m$-dimensional DP set. Its full CI matrix, $\mathbf{H}$, gives rise to an eigenproblem of dimension $K(2m)$,

$$\mathbf{H}\mathbf{C}_i = E_i\mathbf{C}_i \qquad i = 1, 2, \ldots, K(2m). \tag{50}$$

This equation refers to the complete spectrum of $H$, including negative-energy $N$-particle states. Via a nonsingular linear transformation of the one-particle basis set, and a proper arrangement of configuration-state-functions, the left upper corner of $\mathbf{H}$ up to rows and columns of order $K(m)$ can always be made to coincide with the matrix of a no-pair Hamiltonian $\mathbf{H}^{NP}$ constructed just from an $m$ dimensional primitive basis of approximate positive energy eigenstates of a Hamiltonian $h_0$. If $K^-(2m) = K(2m) - K(m)$, according to Eq. (46),

$$E_i^{NP} \leq E_{K^-(2m)+i}, \qquad i > 0, \tag{51}$$

indicating that the eigenvalues $E_i^{NP}$ of relativistic CI calculations with projected bases will always lie *below* the eigenvalues $E_{K^-(2m)+i}$ of the CI matrix $\mathbf{H}$, whatever choice of $h_0$ is made.

The first question about Eq. (51) is what happens if the eigenvalues of order $K^-(2m)+ i$, $i > 0$, are minimized upon general variations of the nonlinear parameters defining the DP basis. The *general behavior* will be illustrated with full CI for $U^{90+}$ $1s^2$ with a
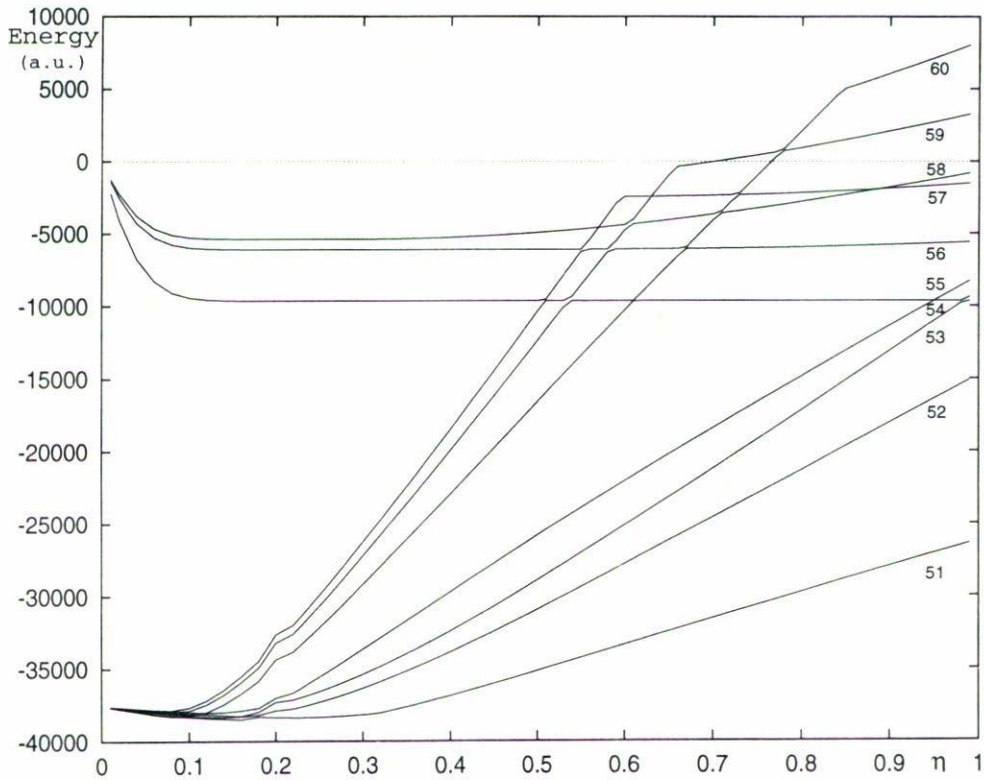
FIGURE 4. Behavior of selected eigenvalues of **H** for $U^{90+}$ $1s^2$ as a function of a scaling parameter $\eta$, exhibiting bound states above $E_{K^-}$ and continuum-dissolution at and below it.

DP basis of twelve $1s_{1/2}$ orbitals [81]. Thus $m = 6$, the CI size is $K(2m) = 78$, and $K^-(2m) = 57$. We use Eqs. (48)–(50) with radial functions

$$P_{n_i lj}(r) = Q_{n_i lj}(r) = r^\gamma e^{-\lambda_i r}, \tag{52}$$

$$\gamma = \sqrt{\kappa^2 - (\alpha Z)^2}, \qquad \lambda_i = \eta a b^i, \qquad i = 1, \dots, 6. \tag{53}$$

We set $b = 1.4$, while $a$ was optimized at the nonrelativistic level. The scaling parameter $\eta$ will be varied between 0 and 1. In Fig. 4 we show eigenvalues of **H** of orders 51 through 60 as a function of $\eta$. For definiteness, $V_{e-e} = e^2 \sum r_{mn}^{-1}$, thus $H$ is taken as the *Dirac-Coulomb* Hamiltonian $H_C$, Eq. (34).

According to the definition of $K^-(2m)$, we must look for a target eigenvalue of order $K^-(2m) + 1 = 58$. However, for $\eta = 1$, $E_{58}$ is seen to be located just below the line signaling the zero of energy (fully ionized system), and high above its expected position around $-9651$ a.u. Furthermore, we find an eigenvalue $E_b$ *and* an eigenfunction $\Psi_b$ closely resembling the sought after $N$-particle electron state, within the first $K^-(2m)$ eigenvalues, initially at position $K_b = 53 \leq K^-(2m)$. The resemblance of $\Psi_b$ with a bound state is linked to a bound character discussed below, associated to a dominant configuration expected to represent it.
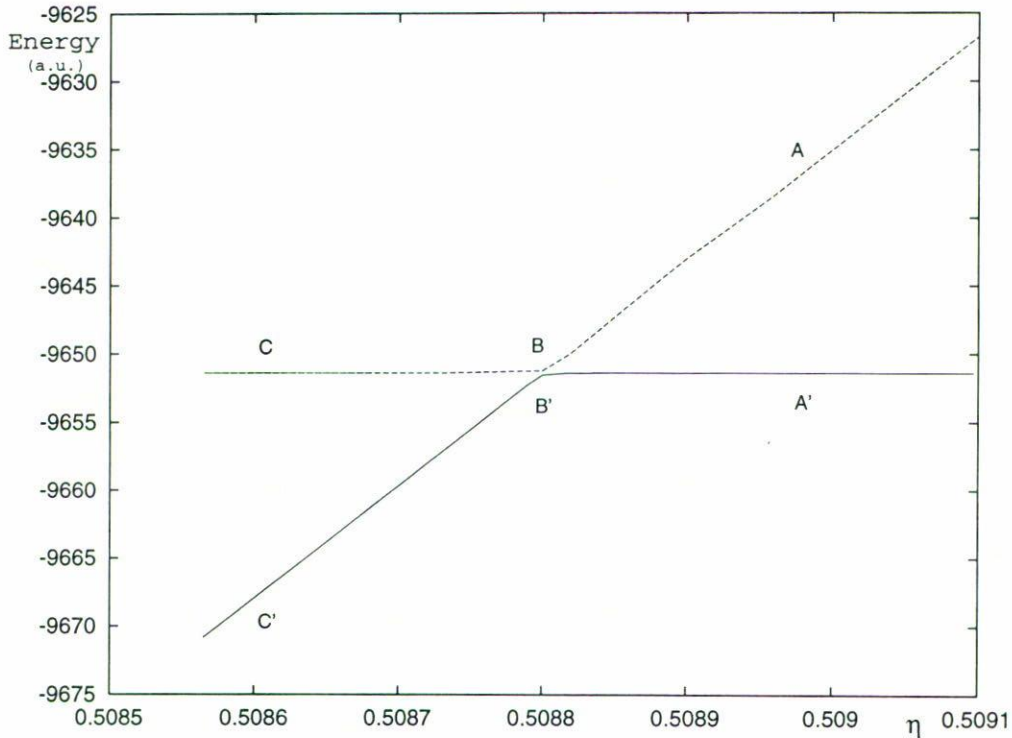
FIGURE 5. Amplification of the neighborhood of the last avoided crossing of Fig. 4.

Now we proceed to vary the scaling parameter $\eta$ characterizing the radial functions $P$ and $Q$, so as to lower as much as possible the target eigenvalue. This corresponds to moving leftwards in Fig. 4. We find that eventually a minimum energy for the target eigenvalue is reached at which point its eigenfunction represents faithfully the lowest state of the given symmetry. In the process in which the original DP basis is being *changed* into a relativistically energy-optimized DP basis, the energy $E_b$ of the state $\Psi_b$ varies slightly, while some of the eigenvalues above begin to approach $E_b$. A bit later, the lowest of them becomes almost *degenerate* with $E_b$. At this point, coinciding with an avoided crossing, there is a transfer of character from one state to another: the lower state exchanges its bound character with the state immediately above. Thereafter, the eigenvalue of order $N_b$, now deprived from its former bound-state character, starts to sink down towards $(N-2)mc^2$, around $-37\,558$ a.u. (after subtracting $Nmc^2$).

We shall now delve into the nature of the variational eigenfunctions. In Fig. 5 we amplify the region of Fig. 4 showing the *last* avoided crossing towards the build up of the lowest bound state, corresponding to $E_{58}$, around $-9651$ a.u. and $\eta = 0.5088$. In the vicinity of points A and A', the eigenvalue of order 58 is appreciably above the eigenvalue of order 57 which is at the approximately correct bound state energy . Points B and B' are very close to the avoided crossing. Towards the left, points C and C' show that while $E_{58}$ stays close to the correct bound state energy, $E_{57}$ starts going down very fast. An examination of the composition of the respective wavefunctions, $\Psi_{57}$ and $\Psi_{58}$, shows how

the bound state character is transferred from level 57 to level 58 as the neighborhood of B and B' is crossed from right to left.

The composition of the wavefunction is conveniently analized using the one-particle basis sets which guarantee a compact representation of the CI wavefunction. In this context, the reduced first-order density matrix $\gamma(1, 1')$,

$$\gamma(1, 1') = N \int \Psi^*(1, 2, \ldots, N) \, \Psi(1', 2, \ldots, N) \, d(2, 3, \ldots, N), \tag{54}$$

plays a central role in nonrelativistic CI [91], as its eigenfunctions $\chi_i$, called *natural orbitals* (NO's),

$$\gamma(1, 1') = \sum n_i \chi_i^*(1) \chi_i(1') \tag{55}$$

provide a fast-convergent one-particle basis for the $N$-electron CI expansion [92], thus affording a compact representation of the wave function. The eigenvalues $n_i$ of $\gamma(1, 1')$, called occupation numbers, are a measure of the importance of $\chi_i$ in a CI expansion expressed in terms of NO's.

In Table I, the dominant configurations of the respective eigenfunctions are shown through the CI coefficients $a$ and $b$:

$$\Psi \approx a[1s(+)^2] + b[2s(+)3s(-)], \tag{56}$$

$$2s(+) = \frac{1}{\sqrt{2}}[2s + 3s], \quad 3s(-) = \frac{1}{\sqrt{2}}[2s - 3s]. \tag{57}$$

In Eqs. (57–58) $1s(+)$, $2s$ and $3s$ denote the first three NO's while $2s(+)$ and $3s(-)$ were constructed from corresponding NO's through Eq. (57) so that they are $(+)$ and $(-)$ orbitals, respectively. (A $(+)$ NO has positive expectation values of $c\vec{\alpha} \cdot \vec{p}$ and of the mass operator $\beta mc^2$.) For $\eta = 0.5090$ the positive bound state orbital $1s(+)$ is almost doubly occupied in level 57 with a very small contribution from the $2s(+)3s(-)$ configuration directly related to continuum-dissolution; meanwhile, level 58 exhibits a complementary orthogonal composition. For $\eta = 0.5088$, both levels show practically equal contributions from the bound-state and continuum-dissolution configurations. Finally, for $\eta = 0.5086$ the bound character has been definitely transferred to level 58, as expected, while level 57 dissolves into $2s(+)3s(-)$.

The values of $\eta$ in the previous paragraph are still far from the optimized value $\eta = 0.2635$ yielding the actual minimum for $E_{58} = -9651.385\,651\,88$. The corresponding eigenfunction for the optimal value of $\eta$ is:

$$\begin{aligned} \Psi_{58} \approx \quad & 0.999999[1s(+)^2] - 0.001388[2s(+)^2] \\ & - 0.000269[3s(+)^2] + 0.000065[4s(-)^2] \\ & - 0.000028[5s(+)^2] + 0.000010[6s(-)^2]. \end{aligned} \tag{58}$$

Its dominant configurations are formed by $(+)$ NO's. Small contributions from $(-)$ NO's are present *only* in configurations with both electrons in the same orbital, whereas

TABLE I. Variational parameter $\eta$, energies and eigenfunctions of levels 57 and 58 in the neighborhood of the last avoided crossing, Fig. 4; energies in a.u., $c=137.0373$.

| $\eta$ | $E_{57}$ | $\Psi_{57}$ |
| | $E_{58}$ | $\Psi_{58}$ |
| --- | --- | --- |
| 0.5090 | $-9651.3874$ | $0.99992[1s(+)^2] + 0.01240[2s(+)3s(-)]$ |
| | $-9638.3541$ | $-0.01240[1s(+)^2] + 0.99992[2s(+)3s(-)]$ |
| 0.5088 | $-9651.5430$ | $0.71593[1s(+)^2] + 0.69817[2s(+)3s(-)]$ |
| | $-9651.2197$ | $0.69817[1s(+)^2] - 0.71593[2s(+)3s(-)]$ |
| 0.5086 | $-9670.8397$ | $0.00831[1s(+)^2] + 0.99997[2s(+)3s(-)]$ |
| | $-9651.3841$ | $0.99996[1s(+)^2] - 0.00831[2s(+)3s(-)]$ |

continuum-dissolution $(+)(-)$ configurations have completely disappeared. This result is consistent with the QED prediction that to fourth-order perturbation theory continuum dissolution terms vanish identically [94]; it also incorporates the expected presence of configurations with both electrons in negative-energy states. In addition, the energy contribution of these $(-)$ NO's, when using DP bases, will always be of positive sign as a consequence of the interleaving theorem.

Many previous workers found these $(-)$ $N$-particle states and concluded that their existence would prevent the occurrence of authentic bound states. Because $H$ is not bound from below, the usual variational theorem cannot be applied to them. However, according to Eq. (51), the eigenvalues $E_{K-+i}$ must be upper bounds to the eigenvalues of the no-pair Hamiltonian. In fact, we find that all these eigenvalues reach real minima corresponding to the ground and successive excited states: they do not dissolve into the continuum as those of order $K^-(2m)$ and below. As $m$ is increased, convergence to an *exact* bound state solution is *always* found; it may be from above, from below, or show oscillatory behavior [90], in contrast with the familiar nonrelativistic situation where convergence is from above. This suggests the existence of a *variational principle* for all states above $K^-(2m)$, for any value of $m$.

A second question about Eq. (51) is how do the eigenvalues of $\mathbf{H}$ and $\mathbf{H}^{NP}$ compare in actual calculations. In Table II we show that constructing $\mathbf{H}^{NP}$ from DHF positive-energy eigenfunctions, the lowest eigenvalue of $\mathbf{H}^{NP}$ for $U^{90+}$ $1s^2$ sinks 3340 $\mu$hartree below $E_{K-+1}$, indicating that the effect of negative-energy one-particle states, included in $\mathbf{H}$ but *not* in $\mathbf{H}^{NP}$ is far from negligible.

Notice that the $K(2m)$ eigenvalues of $\mathbf{H}$ are entirely determined by the DP set, independently of any *a priori* identification of $(+)$ and $(-)$ one-particle bases. Thus, the third question about Eq. (51) is what happens if we *maximize* the energies $E_i^{NP}$ with respect to a nonsingular linear transformation within the entire DP set? It immediately follows that Eq. (51) contains a minimax theorem, whose numerical consequences are being examined [82], including the determination of *best* positive-energy orbitals in calculations

TABLE II. Full CI calculations for $Fe^{24+}$ and $U^{90+}$ $1s^2$ ground states using a DP basis, and an SP basis of positive-energy DHF eigenfunctions. The two calculations use the same nine $s$ Slater-type orbital bases. Energies in a.u., $c=137.035981$ for $Fe^{24+}$, and $c = 137.0373$ for $U^{90+}$.

| Basis | $Fe^{24+}$ | $U^{90+}$ |
|---|---|---|
| DP | $-665.854646$ | $-9651.385503$ |
| (+) DHF orbitals | $-665.854698$ | $-9651.388843$ |

beyond DHF.

Now one can ask a fourth question: is it possible, within a given DP basis, to find an SP basis such that

$$E_1^{SP} = E_{K^-(2m)+1}?\tag{59}$$

In Ref. 93 it is shown this to be the case at the independent-particle-model level of approximation, and this is the reason why our DHF results are in excellent agreement [93] with finite-difference DHF calculations. However, in general, beyond DHF, Eq. (59) cannot be satisfied.

It remains to answer the riddle posed by the Brown-Ravenhall argument concerning continuum dissolution. The time-independent equation for stationary states can be solved with $V_{e-e}$ replaced by $\chi V_{e-e}$, where $\chi$ is varied between 0 and 100, $\chi = 1$ corresponding to the actual physical situation. When considering a true atomic resonance, like nonrelativistic He $2s^2$, the various excited eigenvalues associated with resonant states as a function of $\chi$ show a behavior like the one exhibited on the right side of Fig. 4, with many saddle points and associated wavefunctions undergoing change of character in the vicinity of avoided crossings, similarly as continuum-dissolution states discussed before. Instead, if one returns to the relativistic problem and uses the optimal scaling parameter $\eta = 0.2635$, one gets, for the relevant eigenvalues of order $K^-(2m)+i, i > 0$, as a function of $\chi$, a smooth behavior, *without* avoided crossings, even when $\chi = 100$, one hundred times larger than its actual physical value. This behavior reinforces the argument about the bound character of the pertinent variational eigenfunctions.

Summarizing, after climbing over the first $K^-$ eigenvalues of $\mathbf{H}$, the remaining eigenvalues are upper bounds to the eigenvalues of the no-pair Hamiltonian. Its corresponding eigenfunctions are bonafide bound states, that is, without the Brown-Ravenhall disease. A wealth of numerical results have been obtained thereby [81, 82, 90, 93, 95], including excited states [90]; finite-basis DHF results of numerical quality for *any* open shells, and translation of nonrelativistic into relativistic results [93]; elastic electron scattering factors [95], and various applications in progress.

## 11. DISCUSSION AND OUTLOOK.

One of our aims has been to show that QED plays an important role in the understanding of atomic structure. That is, quantum field theory concepts in atomic physics are

important not just for describing the so called exotic atoms (positronium, muonium, etc.) or for manipulating atomic properties via cavity QED phenomena. Even the simplest atomic systems require for their complete description approximation schemes that are expected to be derivable from quantum field theories let it be QED or its electroweak extension.

Some atomic properties have not a perturbative character while standard quantum field theories are formulated perturbatively. The bound state formalism has been constructed for taking into account some essential properties of the electromagnetic nuclear-electron interaction in a nonperturbative way. Its main deficiency is that it does not include other nuclear effects such as recoil. Fortunately, however, recoil effects are perturbative for standard atomic systems (they are not for other systems such as positronium). This has been exploited in the QED tests with high-$Z$ few-electron atoms that we briefly reviewed in the first sections of this article.

During the development of the bound-state formalism, it was learned that not just nuclear effects can be introduced nonperturbatively. Some interelectronic interaction effects can be taken into account by effective potentials from which a QED formalism can start. Nevertheless, this fact has only been used to evaluate radiative corrections. For more than two electrons, correlation effects are evaluated using many-body Hamiltonians. There are at least two reasons for doing this. One of them is that seventy years of nonrelativistic quantum mechanics have allowed the development of approximate schemes such as the independent particle model which have proven their usefulness in innumerable tests. The other is that the direct evaluation of multiphoton Feynman diagrams in the Furry picture is not a trivial task. In this respect, it would be interesting to formulate QED starting not from one-particle states but from $N$-particle states. This possibility has not been properly studied and it is an alternative which, from the beginning, would recognize atoms as *correlated* bound states. One of the difficulties for developing this formalism is that the properties of an $N$-particle Dirac Hamiltonian are not well known.

After invoking the interleaving theorem to relate the eigenvalues of the no-pair Hamiltonian with those of the complete Hamiltonian, we have found that, contrary to current wisdom, the $N$-body Dirac-Coulomb Hamiltonian does have bound states. We have exemplified this finding with the calculations reported in the last section. This allows to evaluate correlation effects in a nonperturbative way and without referring to one-particle positive-energy projection operators selected *a priori*. We are presently exploring the behavior of $N$-particle Dirac operators and their relationship with QED.

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