

Self-energy Effects on Nuclear Magnetic Resonance Parameters within Quantum Electrodynamics Perturbation Theory

Rodolfo H. Romero and Gustavo A. Aucar

Facultad de Ciencias Exactas, Universidad Nacional del Nordeste, Avenida Libertad 5500 (3400) Corrientes, Argentina. Tel. +54 3783 473931 Fax. +54 3783 473930
E-mail: rromero@exa.unne.edu.ar; gaa@rec.unne.edu.ar

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Abstract: A theory for the calculation of self-energy corrections to the nuclear magnetic parameters is given in this paper. It is based on the S -matrix formulation of bound-state quantum electrodynamics (QED). Explicit expressions for the various terms of the S -matrix are given. The interpretation of the *self-energy*, *one-* and *two-vertex* terms and some perspective for possible future developments are discussed.

Keywords: NMR parameters; Quantum Electrodynamics; S -matrix theory; Self-energy correction; Dirac-Fock perturbation theory.

1 Introduction

Relativistic effects are at the moment starting to be included routinely in calculations of magnetic molecular properties on molecular systems that contain heavy atoms. That is because we are aware of that they are very important in order to predict experimental results.

The usual treatment of molecular properties by theoretical methods is based on classical electrodynamic theory, *i.e.* without resorting to quantized fields. The reason is that most of the relevant terms are included in the perturbed Hamiltonian just using classical fields. Given that the experimental results for magnetic molecular properties have an increasing precision that is in average less than a few percent of its total value it would be important to relax the limitation of using classical fields in our calculations in order to include additional corrections. This is also important from a formal point of view.

Then the next step for precise calculation of molecular properties is related with QED effects. There were some preliminary studies for atomic systems by different groups. Labzowsky, Goidenko and Pyykko found that the bound-state QED contributions to the g -factor of valence ns electrons in alkali metal atoms is as large as 10 % for Rb and less for the other atoms of that series.¹ They also showed that the radiative corrections for the heavy and superheavy atoms can rise up to 0.5% of the ionization energy.² They included QED derived potentials on usual perturbation theory to calculate energy corrections.

Our aim in this paper is to go an step forward trying to describe in some detail a formalism necessary to use when one wants to include QED effects on molecular magnetic properties; even though we have recently worked on the NMR-J spectroscopic parameter by using a different methodology.³ The new scheme presented here can be applied to both spectroscopic parameters mentioned above and is more systematic than the previous one.

In order to include QED effects in calculation of atomic or molecular properties it is possible to work with different formalisms. The formulation of QED we choose to work with is the adiabatic S -matrix approach of Gell-Mann, Low⁴ and Sucher⁵ which was first applied to the bound-state QED by Labzowsky⁶ and later on by Mohr.⁷ This formalism was applied very recently to atomic and highly ionized systems.^{8,9} In our previous work on this field we worked out QED corrections to the NMR-J spectroscopic parameter but without inclusion of radiative corrections which are now treated properly from the outset.

In the next section we give a summary of quantum electrodynamics perturbation theory based on S -matrix formalism. Then we apply that general formalism to the calculation of self-energy corrections to NMR properties. Depending on the external potential we choose (arising from the nuclear magnetic moment or the external static magnetic field) we arrive to J or σ .

2 Quantum electrodynamics perturbation theory

We briefly outline in this section the theory for the calculation of level shifts of bound state electrons interacting with quantized radiation. A more comprehensive description can be found elsewhere.⁷ Bound state quantum electrodynamics is a reformulation of standard QED for free-particles as described in textbooks.¹⁰ It is assumed that Dirac equation with a given classical potential \mathcal{V}

$$[c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2 + \mathcal{V}] \phi_i = \varepsilon_i \phi_i \quad (1)$$

can be solved. The factors $\boldsymbol{\alpha}$ are the 4×4 Dirac matrices which, in the *standard representation*, has the form

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}, \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (2)$$

$\boldsymbol{\sigma}$ are the Pauli matrices, and 0 and 1 represent the null and unit 2×2 matrices. It is convenient to use the set of matrices $\gamma^0 = \beta$ and $\boldsymbol{\gamma} = \beta\boldsymbol{\alpha}$ in order to manifest explicitly the relativistic covariance properties of the Dirac matrices.

The eigenfunctions ϕ_i are taken as the zeroth-order wave functions in terms of which the field operators are built

$$\psi(x) = \sum_{\varepsilon_i > 0} a_i \phi_i(x) + \sum_{\varepsilon_j < 0} b_j^\dagger \phi_j, \quad (3)$$

where a_i (b_j^\dagger) is the annihilation (creation) operator for an electron (a positron) in the state ϕ_i (ϕ_j) of energy $\varepsilon_i > 0$ ($\varepsilon_j < 0$). The Fock operators satisfy the usual anti-commutation relations

$$[a_i, a_j^\dagger]_+ = [b_i, b_j^\dagger]_+ = \delta_{ij}, \quad (4)$$

and zero otherwise.

The interaction between electrons and a quantized electromagnetic field is accounted for through the interaction Hamiltonian

$$H_I(x) = \int d^3x j^\mu(x) A_\mu(x), \quad (5)$$

where $j^\mu(x) = -e\bar{\psi}(x)\gamma^\mu\psi(x)$ is the Dirac 4-current written in terms of the fermion fields and the γ matrices $\gamma^\mu = (\gamma^0, \boldsymbol{\gamma})$, A_μ is the electromagnetic 4-vector potential and $x = (x^0, \mathbf{x})$ is the position 4-vector¹.

For the level shifts calculations, it is convenient to replace the interaction Hamiltonian by an adiabatically damped one

$$H_I^\varepsilon(x) = \int d^3x e^{-\varepsilon|x^0|} j^\mu(x) A_\mu(x). \quad (6)$$

¹Einstein's convention that two repeated Greek indices indicates summation from 0 to 3 is used throughout this paper.

In that case, Gell-Mann, Low⁴ and Sucher⁵ have shown that the energy shift of an unperturbed state $|0\rangle$ is given by

$$\Delta E_0 = \lim_{\epsilon \rightarrow 0, \lambda \rightarrow 1} \frac{i\epsilon\lambda}{2} \frac{\frac{\partial}{\partial \lambda} \langle 0 | S_{\epsilon, \lambda} | 0 \rangle_c}{\langle 0 | S_{\epsilon, \lambda} | 0 \rangle_c} + const. \tag{7}$$

where $S_{\epsilon, \lambda}$ is the S -matrix defined as

$$S_{\epsilon, \lambda} = 1 + \sum_{k=1}^{\infty} \frac{(-i\lambda)^k}{k!} \int d^4x_1 \dots \int d^4x_k T\{H_I^\epsilon(x_1) \dots H_I^\epsilon(x_k)\}. \tag{8}$$

$T\{H_I^\epsilon(x_1) \dots H_I^\epsilon(x_k)\}$ is the *time-ordered product* (i.e., $x_1^0 < x_2^0 < \dots < x_k^0$) of the operators $H_I^\epsilon(x_1) \dots H_I^\epsilon(x_k)$, and $\langle \dots \rangle_c$ represents connected diagrams corresponding to expectation values on the state $|0\rangle$ and it will be implicitly understood in the following. Wick's theorem¹¹ allows to express a T -product of any set of Fock operators $A, B, C, \dots X, Y, Z$ in terms of their *normal ordered* product and one, two, etc. *contractions*,

$$\begin{aligned} T\{ABC \dots XYZ\} &= :ABC \dots XYZ: + : \underbrace{ABC} \dots XYZ: + : \underbrace{ABC} \dots XYZ: + \dots \\ &+ : \underbrace{ABC \dots XYZ}: + \dots \end{aligned} \tag{9}$$

i.e. product of Fock operators with the creation operators placed to the left of the annihilation operators times photon and fermion propagators (represented by the underbraces) defined as

$$S_F(x, y) = \langle T\{\psi(x)\bar{\psi}(y)\} \rangle, \tag{10}$$

$$D_{F\mu\nu}(x, y) = \langle T\{A_\mu(x)A_\nu(y)\} \rangle. \tag{11}$$

The time dependence of the propagators can be made explicit if we write them as follows

$$S_F(x, y) = \int \frac{dE}{2\pi i} S_F(\mathbf{x}, \mathbf{y}; E) e^{-iE(x^0 - y^0)}, \tag{12}$$

$$D_{F\mu\nu}(x, y) = g_{\mu\nu} \int \frac{dk_0}{2\pi i} D_F(\mathbf{x}, \mathbf{y}; k_0) e^{-ik_0(x^0 - y^0)}. \tag{13}$$

The fermion propagator $S_F(\mathbf{x}, \mathbf{y}; E)$ has the following spectral representation⁷

$$S_F(\mathbf{x}, \mathbf{y}; E) = \sum_n \frac{\phi_n(\mathbf{x})\bar{\phi}_n(\mathbf{y})}{E - \epsilon_n(1 - i\delta)}, \tag{14}$$

where δ is an infinitesimal positive quantity and n runs over the complete spectrum of eigenfunctions. Expanding ΔE_0 in power of λ , the energy formula can be written from first to fourth order in the S -matrix as

$$\Delta E_0^{(1)} = \frac{i\epsilon}{2} \langle S^{(1)} \rangle, \tag{15}$$

$$\Delta E_0^{(2)} = \frac{i\epsilon}{2} \left(2\langle S^{(2)} \rangle - \langle S^{(1)} \rangle^2 \right), \tag{16}$$

$$\Delta E_0^{(3)} = \frac{i\epsilon}{2} \left(3\langle S^{(3)} \rangle - 3\langle S^{(1)} \rangle \langle S^{(2)} \rangle + \langle S^{(1)} \rangle^3 \right), \tag{17}$$



Figure 1: Basic self-energy Feynman diagram.

$$\Delta E_0^{(4)} = \frac{i\epsilon}{2} \left(4\langle S^{(4)} \rangle - 4\langle S^{(1)} \rangle \langle S^{(3)} \rangle - 2\langle S^{(2)} \rangle^2 + 4\langle S^{(1)} \rangle^2 \langle S^{(2)} \rangle - \langle S^{(1)} \rangle^4 \right). \quad (18)$$

It has been shown⁷ that, for classical external potentials V and one-electron atoms in the state a , the first and second order level shift formula reduces to the well known expressions from standard perturbation theory

$$\Delta E_a^{(1)} = V_{aa} \quad (19)$$

$$\Delta E_a^{(2)} = \sum_{E_n \neq E_a} V_{an} \frac{1}{E_a - E_n} V_{na}. \quad (20)$$

As an application of the third order formula, Blundell *et al.*⁸ calculated self-energy corrections in atomic systems in the presence of an external potential. In the next section, we use the fourth order energy expression $\Delta E_0^{(4)}$ to obtain self-energy corrections to the NMR parameters.

3 Self-energy effects on NMR properties

In this section, the S -matrix theory outlined in the previous section is applied to obtain expressions for the self-energy corrections to the NMR parameters J and σ . The self-energy correction corresponds to the level shifts due to the interaction of an electron with itself *via* one photon exchange (Fig. 1). For the problem we are tackling, we need to consider this type of diagrams in addition to the interaction with two external potentials, namely, those coming from the interaction of an electron with the magnetic moments $\boldsymbol{\mu}$ of two different nuclei (in the case of the tensor J) or the electron with a nucleus and the external magnetic field \mathbf{B} (in the case of the nuclear magnetic shielding σ).

Hence, we consider the electromagnetic 4-potential as the sum of a quantized potential A_μ plus a classical one $(\varphi, 0, 0, 0)$ and take the Dirac-Fock ground state $|DF\rangle$ as the unperturbed state $|0\rangle$. Then, the interaction Hamiltonian splits in $H_I = H_I^A + H_I^B$, where

$$H_I^A = e \int d^3x \bar{\psi}(x) \gamma^\mu A_\mu \psi(x), \quad (21)$$

$$H_I^B = \int d^3x \bar{\psi}(x) V(x) \psi(x), \quad (22)$$

and $V(x) = e\gamma^0\varphi(x) = \gamma^0U(x)$. In order to discuss simultaneously both J and σ we assume $V = V_N + V_B$, where

$$V_N(\mathbf{r}) = -e\boldsymbol{\gamma} \cdot \boldsymbol{\mu}_N \times \frac{\mathbf{r}_N}{r_N^3} \tag{23}$$

$$V_B(\mathbf{r}) = -e\boldsymbol{\gamma} \cdot \frac{\mathbf{B} \times \mathbf{r}}{2}, \tag{24}$$

such that the proper potential should be taken for the property of interest.

Since we are interested in properties quadratic in the external potential V , the $\Delta E_0^{(4)}$ expression can be written as

$$\Delta E_0^{(4)} = 2i\epsilon \left(\langle S^{(4)} \rangle - \langle S^{(2a)} \rangle \langle S^{(2b)} \rangle + \langle S^{(1)} \rangle^2 \langle S^{(2a)} \rangle - \langle S^{(1)} \rangle \langle S^{(3)} \rangle \right), \tag{25}$$

where

$$\langle S_{\epsilon\lambda}^{(1)} \rangle = -i\lambda \int d^4x e^{-\epsilon|x^0|} \langle T \{ (:\bar{\psi}V\psi:)_x \} \rangle \tag{26}$$

$$\begin{aligned} \langle S_{\epsilon\lambda}^{(2a)} \rangle &= -\frac{\lambda^2 e^2}{2} \int d^4x \int d^4y e^{-\epsilon|x^0|} e^{-\epsilon|y^0|} \\ &\times \langle T \{ (:\bar{\psi}\gamma^\mu A_\mu\psi:)_x (:\bar{\psi}\gamma^\nu A_\nu\psi:)_y \} \rangle \end{aligned} \tag{27}$$

$$\begin{aligned} \langle S_{\epsilon\lambda}^{(2b)} \rangle &= -\frac{\lambda^2}{2} \int d^4x \int d^4y e^{-\epsilon|x^0|} e^{-\epsilon|y^0|} \\ &\times \langle T \{ (:\bar{\psi}V\psi:)_x (:\bar{\psi}V\psi:)_y \} \rangle \end{aligned} \tag{28}$$

$$\begin{aligned} \langle S_{\epsilon\lambda}^{(3)} \rangle &= \frac{i\lambda^3 e^2}{3} \int d^4x \int d^4y \int d^4z e^{-\epsilon|x^0|} e^{-\epsilon|y^0|} e^{-\epsilon|z^0|} \\ &\times \langle T \{ (:\bar{\psi}\gamma^\mu A_\mu\psi:)_x (:\bar{\psi}\gamma^\nu A_\nu\psi:)_y (:\bar{\psi}V\psi:)_z \} \rangle \end{aligned} \tag{29}$$

$$\begin{aligned} \langle S_{\epsilon\lambda}^{(4)} \rangle &= \frac{\lambda^4 e^2}{4} \int d^4w \int d^4x \int d^4y \int d^4z e^{-\epsilon|w^0|} e^{-\epsilon|x^0|} e^{-\epsilon|y^0|} e^{-\epsilon|z^0|} \\ &\times \langle T \{ (:\bar{\psi}V\psi:)_w (:\bar{\psi}\gamma^\mu A_\mu\psi:)_x (:\bar{\psi}\gamma^\nu A_\nu\psi:)_y (:\bar{\psi}V\psi:)_z \} \rangle \end{aligned} \tag{30}$$

Note that $S^{(2a)}$ and $S^{(2b)}$ represent the terms of the second order S -matrix containing only quantized and classical potentials, respectively. It should be also stressed that even when we are treating a many-electron system, the use of the approximation of independent particles and, hence, the lack of dynamical correlation in the wave functions, allows us to use all the formal machinery devised for one-electron calculations.

Let us consider separately the different contributions to the S -matrix.

3.1 First order

As an illustration of the use of the level shift formulas, let us consider in detail the calculations of the first few orders of the S -matrix. To first order, writing explicitly the time dependence, and taking into account that the state $|0\rangle$ has no positrons, we get

$$\begin{aligned} \langle S_{\epsilon\lambda}^{(1)} \rangle &= -i\lambda \sum_{ij} \int d^3x \bar{\phi}_i(\mathbf{x}) V(\mathbf{x}) \phi_j(\mathbf{x}) \\ &\quad \times \int dx^0 e^{-\epsilon|x^0|} e^{i(\epsilon_i - \epsilon_j)x^0} \langle : a_i^\dagger a_j : \rangle \\ &= -i\lambda \sum_{ij} U_{ij} \frac{2\epsilon}{\epsilon^2 + (\epsilon_i - \epsilon_j)^2} \langle : a_i^\dagger a_j : \rangle \end{aligned} \tag{31}$$

For the Dirac-Fock state $|0\rangle$, $\langle : a_i^\dagger a_j : \rangle = \delta_{ij}$, where i must be an occupied state, say, α . Then,

$$\langle S_{\epsilon\lambda}^{(1)} \rangle = -\frac{2i\lambda}{\epsilon} \sum_{\alpha}^{occ} U_{\alpha\alpha}, \tag{32}$$

that is, $\Delta E_0^{(1)} = \sum_{\alpha}^{occ} U_{\alpha\alpha}$, which is a generalization of the one-electron case.

3.2 Second order

In this section we shall consider in some detail the calculation of the terms $S_{\epsilon\lambda}^{(2a)}$ and $S_{\epsilon\lambda}^{(2b)}$, because their treatment involves some general procedures to be applied in the more complicate higher order terms.

3.2.1 Term $S_{\epsilon\lambda}^{(2a)}$

Application of the Wick theorem to the product $T\{H_{I\epsilon}^A(x)H_{I\epsilon}^A(y)\}$ gives one- and two-electron operators. The one-electron term $2\gamma^\mu D_F(x,y)S_F(x,y)\gamma_\mu : \bar{\psi}(x)\psi(y) :$ is related to the self-energy of the DF-occupied states and is the only term to be included in $S_{\epsilon\lambda}^{(2a)}$. The two-electron term is not relevant for the calculations involved here since it gives a contribution related to one-photon exchange interaction between two-electrons, namely, the *Coulomb-Breit* interaction.

As in the first order case, the expectation value $\langle : \bar{\psi}(x)\psi(y) : \rangle$ becomes a summation over occupied states α . Integration over time variable x^0 gives

$$\int dx^0 e^{-\epsilon|x^0|} e^{-i(k_0 + E - \epsilon_\alpha)x^0} = \Delta_\epsilon(k_0 + E - \epsilon_\alpha) \tag{33}$$

and a similar result for the integration over y^0 , where

$$\Delta_\epsilon(k_0 + E - \epsilon_\alpha) = \frac{2\epsilon}{\epsilon^2 + (k_0 + E - \epsilon_\alpha)^2} \tag{34}$$

is a function such that

$$\Delta_\epsilon(E) \begin{cases} = 2/\epsilon = \mathcal{O}(\epsilon^{-1}), & E = 0, \\ \simeq 2\epsilon/E^2 = \mathcal{O}(\epsilon), & E \neq 0. \end{cases} \quad (35)$$

Recalling that at the end of the calculations we take $\epsilon \rightarrow 0$, the roots $u = 0$ of the argument of $\Delta_\epsilon(u)$ determine the most relevant energy regions for the integrals over E . So, for $S_{\epsilon\lambda}^{(2a)}$, the energy denominator emphasize the region $E = \epsilon_\alpha - k_0$ and we can approximate the integral over E by evaluating the propagator $S(\mathbf{x}, \mathbf{y}; E)$ at that energy value. Hereafter, this will be a general strategy for the evaluation of those integrals. Hence,

$$\langle S_{\epsilon\lambda}^{(2a)} \rangle = \lambda^2 \sum_\alpha^{occ} \int \frac{dE}{2\pi i} \left[\frac{2\epsilon}{\epsilon^2 + (k_0 + E - \epsilon_\alpha)^2} \right]^2 \Sigma_{\alpha\alpha}(\epsilon_\alpha), \quad (36)$$

where the *self-energy* insertion $\Sigma_{mn}(\epsilon)$ is defined by

$$\Sigma_{mn}(\epsilon) = -e^2 \int d^3x \int d^3y \int \frac{dk_0}{2\pi i} \bar{\phi}_m(\mathbf{x}) \gamma^\mu D_F(\mathbf{x}, \mathbf{y}; k_0) S_F(\mathbf{x}, \mathbf{y}; \epsilon - k_0) \gamma_\mu \phi_n(\mathbf{y}). \quad (37)$$

that is,

$$\langle S_{\epsilon\lambda}^{(2a)} \rangle = \frac{\lambda^2}{i\epsilon} \sum_\alpha^{occ} \Sigma_{\alpha\alpha}(\epsilon_\alpha) \quad (38)$$

3.2.2 Term $S_{\epsilon\lambda}^{(2b)}$

The time-ordered product $T\{H_{I\epsilon}^B(x)H_{I\epsilon}^B(y)\}$ has also contributions from one- and two-electron operators

$$\begin{aligned} & 2 \sum_{ij} \bar{\phi}_i(x) V(x) S_F(x, y) V(y) \phi_j(x) a_i^\dagger a_j \\ & + \sum_{ijkl} \bar{\phi}_i(x) V(x) \phi_j(x) \bar{\phi}_k(y) V(y) \phi_l(y) a_i^\dagger a_k^\dagger a_l a_j. \end{aligned} \quad (39)$$

Inserting Eq. (39) into the expression (28) for $S_{\epsilon\lambda}^{(2b)}$, the integration over the time variables gives

$$\Delta_\epsilon(E + k_0 - \epsilon_i) \Delta_\epsilon(E + k_0 - \epsilon_j) \quad (40)$$

for the first (one-electron) term; while

$$\Delta_\epsilon(k_0 + \epsilon_j - \epsilon_i) \Delta_\epsilon(k_0 + \epsilon_k - \epsilon_l) \quad (41)$$

for the two-electron one. Furthermore, for the DF ground state, $\langle a_i^\dagger a_j \rangle = \delta_{ij}$ and $\langle a_i^\dagger a_k^\dagger a_l a_j \rangle = \delta_{ij} \delta_{kl} - \delta_{il} \delta_{kj}$, j and l being occupied orbitals, say, α and β . Hence, the Δ_ϵ -functions emphasize,

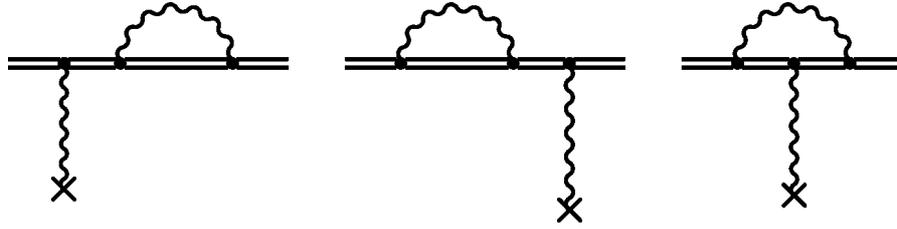


Figure 2: Feynman diagrams *side left* (L), *side right* (R), and *vertex* (V) for self-energy correction corresponding to the $S_{\epsilon\lambda}^{(3)}$ term.

respectively, the regions $E = \epsilon_\alpha - k_0$ and $k_0 = \epsilon_\alpha - \epsilon_\beta$ of the integrals over E and k_0 . Then, $S_{\epsilon\lambda}^{(2b)}$ gives

$$S_{\epsilon\lambda}^{(2b)} = 2\lambda^2\epsilon^2 \sum_{\alpha \neq \beta} \frac{U_{\alpha\beta}U_{\beta\alpha}}{[\epsilon^2 + (\epsilon_\alpha - \epsilon_\beta)^2]^2} + \lambda^2 \sum_{\alpha l} U_{\alpha l}U_{l\alpha} \int \frac{dE}{2\pi i} \frac{1}{E - \epsilon_l(1 - i\delta)} \left[\frac{2\epsilon}{\epsilon^2 + (E - \epsilon_\alpha)^2} \right]^2, \tag{42}$$

where we have replaced the fermion propagator by its spectral representation, Eq. (14). This is a common technique used throughout this paper, and we use it repeatedly in the following sections, for the calculation of higher order terms. It should be noted that the first term of the previous Eq. is of order $\mathcal{O}(\epsilon^2)$ because $\alpha \neq \beta$. Therefore, it does not contribute to the energy shift and, hereafter, it will be disregarded.

Finally,

$$\begin{aligned} \langle S^{(2b)} \rangle &= -2\frac{\lambda^2}{\epsilon^2} \sum_{\alpha l_\alpha} U_{\alpha l_\alpha}U_{l_\alpha\alpha} \\ &+ \lambda^2 \sum_{\alpha l'_\alpha} U_{\alpha l'_\alpha}U_{l'_\alpha\alpha} \left[\frac{\text{sg}(\epsilon_{l'_\alpha})}{(\epsilon_\alpha - \epsilon_{l'_\alpha})^2} + \frac{1}{i\epsilon} \frac{1}{\epsilon_\alpha - \epsilon_{l'_\alpha}} \right]. \end{aligned} \tag{43}$$

where l_α (l'_α) represents states degenerate (non-degenerate) with α .

3.3 Third order

Third order S -matrix, Eq. (29) produces one- and two-electron operators. The former comes from the diagrams depicted in Fig. 2, while the later are product of $S^{(1)}$ times $S^{(2a)}$, *i.e.*, a diagram with two electron lines, one of them interacting with the external field and the other having a self-energy graph (Fig. 1).

Diagrams of Fig. 2 have been previously considered⁸ in the calculation of self-energy corrections in atomic systems in the presence of an external potential. They were named *left-side* (L), *right-*

side (R) and vertex (V) terms. Following the same lines as the calculation of first and second order terms, we get expressions which represent many-electron generalizations of those from Ref.⁸

$$\begin{aligned} \langle S_L^{(3)} \rangle &= i\lambda^3 e^2 \sum_{\alpha}^{occ} \int d^3x \int d^3y \int d^3z \int \frac{dk_0}{2\pi i} \int \frac{dE_1}{2\pi i} \int \frac{dE_2}{2\pi i} \\ &\times \bar{\phi}_{\alpha}(\mathbf{x}) V(\mathbf{z}) S_F(\mathbf{z}, \mathbf{x}; E_1) \gamma^{\mu} D_F(\mathbf{x}, \mathbf{y}; k_0) \\ &\times S_F(\mathbf{x}, \mathbf{y}; E_2) \gamma_{\mu} \phi_{\alpha}(\mathbf{y}) \Delta_{\epsilon}(E_2 + k_0 - E_1) \\ &\times \Delta_{\epsilon}(E_2 + k_0 - \epsilon_{\alpha}) \Delta_{\epsilon}(E_1 - \epsilon_{\alpha}) \end{aligned} \quad (44)$$

$$\begin{aligned} \langle S_R^{(3)} \rangle &= i\lambda^3 e^2 \sum_{\alpha}^{occ} \int d^3x \int d^3y \int d^3z \int \frac{dk_0}{2\pi i} \int \frac{dE_1}{2\pi i} \int \frac{dE_2}{2\pi i} \\ &\times \bar{\phi}_{\alpha}(\mathbf{x}) \gamma^{\mu} D_F(\mathbf{x}, \mathbf{y}; k_0) S_F(\mathbf{x}, \mathbf{y}; E_1) \gamma_{\mu} \\ &\times S_F(\mathbf{y}, \mathbf{z}; E_2) V(\mathbf{z}) \phi_{\alpha}(\mathbf{z}) \Delta_{\epsilon}(E_2 - \epsilon_{\alpha}) \\ &\times \Delta_{\epsilon}(E_1 + k_0 - E_2) \Delta_{\epsilon}(E_1 + k_0 - \epsilon_{\alpha}) \end{aligned} \quad (45)$$

$$\begin{aligned} \langle S_V^{(3)} \rangle &= i\lambda^3 e^2 \sum_{\alpha}^{occ} \int d^3x \int d^3y \int d^3z \int \frac{dk_0}{2\pi i} \int \frac{dE_1}{2\pi i} \int \frac{dE_2}{2\pi i} \\ &\times \bar{\phi}_{\alpha}(\mathbf{x}) \gamma^{\mu} D_F(\mathbf{x}, \mathbf{y}; k_0) S_F(\mathbf{x}, \mathbf{y}; E_1) V(\mathbf{z}) \\ &\times S_F(\mathbf{z}, \mathbf{y}; E_2) \gamma_{\mu} \phi_{\alpha}(\mathbf{y}) \Delta_{\epsilon}(E_1 + k_0 - \epsilon_{\alpha}) \\ &\times \Delta_{\epsilon}(E_2 + k_0 - \epsilon_{\alpha}) \Delta_{\epsilon}(E_1 - E_2). \end{aligned} \quad (46)$$

The Δ_{ϵ} -functions favor $E_1 = \epsilon_{\alpha}$ and $E_2 = \epsilon_{\alpha}$ in $S_L^{(3)}$ and $S_R^{(3)}$, respectively. So, if we proceed, as in the previous lower orders calculations, to replace the fermion propagators by its spectral representations, the whole expression diverges. However, $S_V^{(3)}$ does not suffer of this problem because the arguments of the Δ_{ϵ} -functions does not vanish at any energy eigenvalue ϵ_i . Then, a special treatment must be given to the side terms, while $S_V^{(3)}$ can be handled as before to give

$$\langle S_V^{(3)} \rangle = \frac{2i\lambda^3}{3\epsilon} \sum_{\alpha}^{occ} \Lambda_{\alpha\alpha}(\epsilon_{\alpha}), \quad (47)$$

where the vertex insertion $\Lambda_{nm}(\epsilon)$ is defined by

$$\begin{aligned} \Lambda_{nm}(\epsilon) &= -e^2 \int d^3x \int d^3y \int d^3z \int \frac{dk_0}{2\pi i} \bar{\phi}_m(\mathbf{x}) \gamma^{\mu} D_F(\mathbf{x}, \mathbf{y}; k_0) S_F(\mathbf{x}, \mathbf{z}; \epsilon \\ &- k_0) V(\mathbf{z}) S_F(\mathbf{z}, \mathbf{y}; \epsilon - k_0) \gamma_{\mu} \phi_n(\mathbf{y}). \end{aligned} \quad (48)$$

Inserting those terms of the spectral representation of the fermion propagators, Eq. (14), which are non degenerate with the state α , the calculations follows the same steps of the vertex term

and we get

$$\langle S_L^{(3a)} \rangle = \frac{2i\lambda^3}{3\epsilon} \sum_{\alpha}^{occ} \sum_{\varepsilon_l \neq \varepsilon_{\alpha}} U_{\alpha l} \frac{1}{\varepsilon_{\alpha} - \varepsilon_l} \Sigma_{l\alpha}(\varepsilon_{\alpha}). \tag{49}$$

A similar expression for the right term is

$$\langle S_R^{(3a)} \rangle = \frac{2i\lambda^3}{3\epsilon} \sum_{\alpha}^{occ} \sum_{\varepsilon_l \neq \varepsilon_{\alpha}} \Sigma_{\alpha l}(\varepsilon_{\alpha}) \frac{1}{\varepsilon_{\alpha} - \varepsilon_l} U_{l\alpha} \tag{50}$$

To handle those terms of Eq. (14) corresponding to states degenerates with α , we expand the second propagator in power series around $E = \varepsilon_{\alpha} - k_0$ to first order; for example, in the left side term

$$\begin{aligned} S_F(\mathbf{x}, \mathbf{y}; E_2) &\simeq S_F(\mathbf{x}, \mathbf{y}; \varepsilon_{\alpha} - k_0) \\ &+ (E_2 - \varepsilon_{\alpha} + k_0) \times S'_F(\mathbf{x}, \mathbf{y}; \varepsilon_{\alpha} - k_0), \end{aligned} \tag{51}$$

where

$$\begin{aligned} S'_F(\mathbf{x}, \mathbf{y}; \varepsilon_{\alpha} - k_0) \\ = - \int d^3w S_F(\mathbf{x}, \mathbf{w}; \varepsilon_{\alpha} - k_0) \gamma^0 S_F(\mathbf{w}, \mathbf{y}; \varepsilon_{\alpha} - k_0). \end{aligned} \tag{52}$$

The first term of Eq. (51), combined with the part of the spectral representation of the propagator (14) containing states α' degenerate with α ($\varepsilon_{\alpha'} = \varepsilon_{\alpha}$) divergent at $E = \varepsilon_{\alpha} - k_0$, gives

$$\langle S_L^{(3b)} \rangle = -\frac{i\lambda^3}{\epsilon^2} \sum_{\alpha}^{occ} \sum_{\alpha'} U_{\alpha\alpha'} \Sigma_{\alpha'\alpha} \tag{53}$$

$$\langle S_R^{(3b)} \rangle = -\frac{i\lambda^3}{\epsilon^2} \sum_{\alpha}^{occ} \sum_{\alpha'} \Sigma_{\alpha\alpha'} U_{\alpha'\alpha} \tag{54}$$

Finally, the last term of the expansion (51), together with those from the representation (14) corresponding to states α' , give rise to the so-called *derivative terms*⁷

$$\begin{aligned} \langle S_L^{(3c)} \rangle &= \frac{i\lambda^3 e^2}{3\epsilon} \sum_{\alpha}^{occ} \sum_{\alpha'} U_{\alpha\alpha'} \int d^3w \int d^3x \int d^3y \int \frac{dk_0}{2\pi i} \\ &\times D_F(\mathbf{x}, \mathbf{y}; k_0) \bar{\phi}_{\alpha'}(\mathbf{x}) \gamma^{\mu} S_F(\mathbf{x}, \mathbf{w}; \varepsilon_{\alpha} - k_0) \gamma^0 \\ &\times S_F(\mathbf{w}, \mathbf{y}; \varepsilon_{\alpha} - k_0) \gamma_{\mu} \phi_{\alpha}(\mathbf{y}), \end{aligned} \tag{55}$$

and

$$\begin{aligned} \langle S_R^{(3c)} \rangle &= \frac{i\lambda^3 e^2}{3\epsilon} \sum_{\alpha} \sum_{\alpha'}^{occ} \int d^3w \int d^3x \int d^3y \int \frac{dk_0}{2\pi i} \\ &\times D_F(\mathbf{x}, \mathbf{y}; k_0) \bar{\phi}_{\alpha}(\mathbf{x}) \gamma^{\mu} S_F(\mathbf{x}, \mathbf{w}; \epsilon_{\alpha} - k_0) \gamma^0 \\ &\times S_F(\mathbf{w}, \mathbf{y}; \epsilon_{\alpha} - k_0) \gamma_{\mu} \phi_{\alpha'}(\mathbf{y}) U_{\alpha'\alpha} \end{aligned} \quad (56)$$

It is worth to mention the symmetry between both side terms.

3.4 Fourth order

Following the same procedure as before, we get the following contributions to $S^{(4)}$

$$S^{(4)} = S_{VV}^{(4)} + S_{LV}^{(4)} + S_{VR}^{(4)} + S_{LR}^{(4)} + S_{LL}^{(4)} + S_{RR}^{(4)}, \quad (57)$$

corresponding to the Feynman diagrams of Fig. 3, where

$$\begin{aligned} \langle S_i^{(4)} \rangle &= \lambda^4 e^2 \sum_{\alpha} \int d^4w \int d^4x \int d^4y \int d^4z \\ &\times e^{-\epsilon|w^0|} e^{-\epsilon|x^0|} e^{-\epsilon|y^0|} e^{-\epsilon|z^0|} M_i, \end{aligned} \quad (58)$$

and M_i ($i = VV, LV, VR, LR, LL, RR$) is defined as follows

$$\begin{aligned} M_{VV} &= \bar{\phi}_{\alpha}(x) \gamma^{\mu} D_F(x, y) S_F(x, w) V(w) S_F(w, z) V(z) S_F(z, y) \gamma_{\mu} \phi_{\alpha}(y). \\ M_{LV} &= \bar{\phi}_{\alpha}(w) V(w) S_F(w, x) \gamma^{\mu} D_F(x, y) S_F(x, z) V(z) S_F(z, y) \gamma_{\mu} \phi_{\alpha}(y) \\ M_{VR} &= \bar{\phi}_{\alpha}(x) \gamma^{\mu} D_F(x, y) S_F(x, w) V(w) S_F(w, y) \gamma_{\mu} S_F(y, z) V(z) \phi_{\alpha}(z) \\ M_{LR} &= \bar{\phi}_{\alpha}(w) V(w) S_F(w, x) \gamma^{\mu} D_F(x, y) S_F(x, y) \gamma_{\mu} S_F(y, z) V(z) \phi_{\alpha}(z) \\ M_{LL} &= \bar{\phi}_{\alpha}(w) V(w) S_F(w, z) V(z) S_F(z, x) \gamma^{\mu} D_F(x, y) S_F(x, y) \gamma_{\mu} \phi_{\alpha}(y) \\ M_{RR} &= \bar{\phi}_{\alpha}(x) \gamma^{\mu} D_F(x, y) S_F(x, y) \gamma_{\mu} S_F(y, w) V(w) S_F(w, z) V(z) \phi_{\alpha}(z) \end{aligned} \quad (59)$$

The subscripts (L), (R) and (V) have the same meaning as those from third order terms $S^{(3)}$. Integration over time variables gives products of Δ_{ϵ} -functions emphasizing the energy regions detailed in Table 1. As it is shown there, the relevant point for the energy landscape in the VV term correspond to the value $\epsilon_{\alpha} - k_0$ which is not a pole for any of the propagators. Hence, the term $S_{VV}^{(4)}$ becomes fairly convergent. The contributions $S_{LV}^{(4)}$ and $S_{VR}^{(4)}$, however, contain one fermion propagator diverging at the relevant point ϵ_{α} . Finally, the contributions $S_{LR}^{(4)}$, $S_{LL}^{(4)}$ and $S_{RR}^{(4)}$ have two divergent propagators at the occupied orbital energies. Then, the term $S_{VV}^{(4)}$ can be

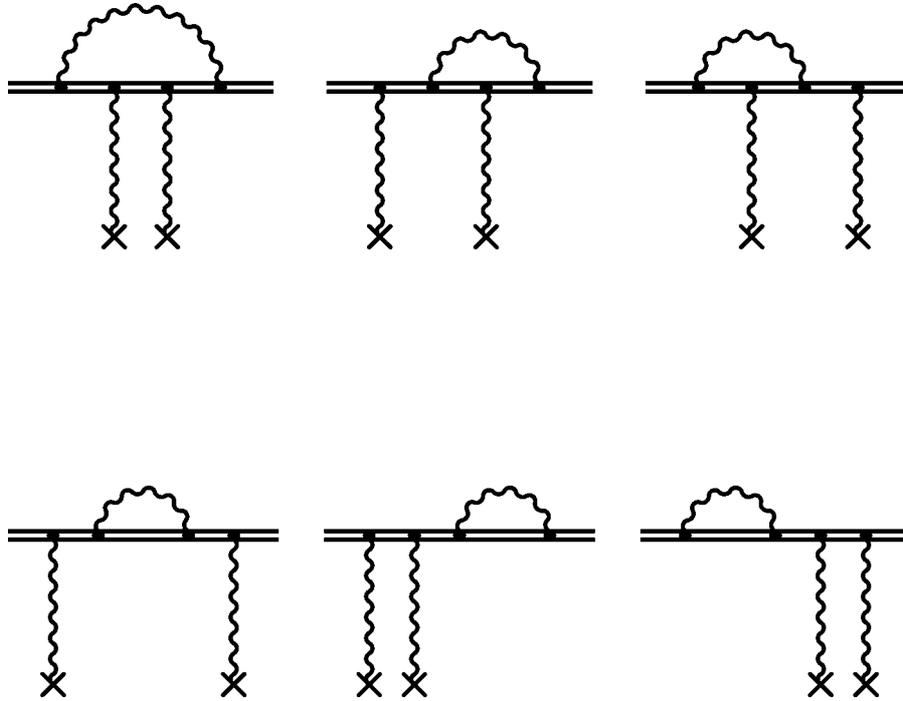


Figure 3: Fourth order Feynman diagrams *vertex-vertex* (VV), *left-vertex* (LV), *vertex-right* (VR), *left-right* (LR), *left-left* (LL) and *right-right* (RR) contributing to self-energy correction quadratic in the external field corresponding to the $S_{\epsilon\lambda}^{(4)}$ term.

Table 1: Energy regions emphasized by the Δ_ϵ -functions after integration over time variables in the contributions to $S^{(4)}$. See text after Eq. (58)

Term	Leading energy regions
VV	$E_1 = E_2 = E_3 = \epsilon_\alpha - k_0$
LV	$E_2 = E_3 = \epsilon_\alpha - k_0, \quad E_1 = \epsilon_\alpha$
VR	$E_1 = E_2 = \epsilon_\alpha - k_0, \quad E_3 = \epsilon_\alpha$
LR	$E_2 = \epsilon_\alpha - k_0, \quad E_1 = E_3 = \epsilon_\alpha$
LL	$E_3 = \epsilon_\alpha - k_0, \quad E_1 = E_2 = \epsilon_\alpha$
RR	$E_1 = \epsilon_\alpha - k_0, \quad E_2 = E_3 = \epsilon_\alpha$

calculated after some long but straightforward manipulations, to give

$$\begin{aligned} \langle S_{VV}^{(4)} \rangle &= \frac{ie^2\lambda^4}{2\epsilon} \sum_{\alpha} \int d^3w \int d^3x \int d^3y \int d^3z \int \frac{dk_0}{2\pi i} \\ &\times \bar{\phi}_{\alpha}(\mathbf{x})\gamma^{\mu}D_F(\mathbf{x}, \mathbf{y}; k_0)S_F(\mathbf{x}, \mathbf{w}; \epsilon_{\alpha} - k_0)V(\mathbf{w}) \\ &\times S_F(\mathbf{w}, \mathbf{z}; \epsilon_{\alpha} - k_0)V(\mathbf{z})S_F(\mathbf{z}, \mathbf{y}; \epsilon_{\alpha} - k_0)\gamma_{\mu}\phi_{\alpha}(\mathbf{y}) \end{aligned} \tag{60}$$

The other contributions, however, require the use of the power expansion (51) for the propagators converging at ϵ_{α} , while separating the states degenerate with α in the spectral representation (14) for those propagators diverging at ϵ_{α} .

So, we have a term arising from the states l non-degenerate with α

$$\langle S_{LV}^{(4)} \rangle_{non-deg} = -\frac{i\lambda^4}{2\epsilon} \sum_{\alpha} \sum_{\substack{occ \\ \epsilon_l \neq \epsilon_{\alpha}}} U_{\alpha l} \frac{1}{\epsilon_{\alpha} - \epsilon_l} \Lambda_{l\alpha}(\epsilon_{\alpha}), \tag{61}$$

plus a term derived from states α' degenerate with α ,

$$\langle S_{LV}^{(4)} \rangle_{deg} = -\frac{2\lambda^4}{3\epsilon^2} \sum_{\alpha} \sum_{\substack{occ \\ \epsilon_{\alpha} = \epsilon_{\alpha'}}} U_{\alpha\alpha'} \Lambda_{\alpha'\alpha}(\epsilon_{\alpha}), \tag{62}$$

with the non divergent (at ϵ_{α}) propagators evaluated at $\epsilon_{\alpha} - k_0$ in both cases. On the other hand, taking the derivative term (51) from one propagator and evaluating the other at $\epsilon_{\alpha} - k_0$ it gives

$$\begin{aligned} \langle S_{LV}^{(4)} \rangle_{deriv} &= -\frac{i\lambda^4 e^2}{3\epsilon} \sum_{\alpha\alpha'} \int d^3w \int d^3x \int d^3y \int d^3z \int \frac{dk_0}{2\pi i} U_{\alpha\alpha'} \\ &\times \bar{\phi}_{\alpha'}(\mathbf{x})\gamma^{\mu}D_F(\mathbf{x}, \mathbf{y}; k_0) \left[S_F(\mathbf{x}, \mathbf{w}; \epsilon_{\alpha} - k_0)\gamma^0 \right. \\ &\times S_F(\mathbf{w}, \mathbf{z}; \epsilon_{\alpha} - k_0)V(\mathbf{z})S_F(\mathbf{z}, \mathbf{y}; \epsilon_{\alpha} - k_0) \\ &+ S_F(\mathbf{x}, \mathbf{z}; \epsilon_{\alpha} - k_0)V(\mathbf{z})S_F(\mathbf{z}, \mathbf{w}; \epsilon_{\alpha} - k_0)\gamma^0 \\ &\times \left. S_F(\mathbf{w}, \mathbf{y}; \epsilon_{\alpha} - k_0)\gamma_{\mu} \right] \phi_{\alpha}(\mathbf{y}). \end{aligned} \tag{63}$$

Finally, there is also a term arising from the derivative term in both propagators. However, that term becomes of the order $\mathcal{O}(\epsilon^0)$, so it does not give any level shift and can be disregarded. The $S_{VR}^{(4)}$ contribution can be split similarly, too.

In the treatment of the terms $S_{LR}^{(4)}$, $S_{LL}^{(4)}$ and $S_{RR}^{(4)}$, we separate the degenerate states α' and α'' from the spectral representation of the two propagators which diverge at ϵ_{α} , and expand the other one according to (51). We shall not give here the details of the resulting terms which are rather

involved; but, as an illustration, we can consider, for example, those parts of the propagators depending on the states l and n having energies $\varepsilon_l \neq \varepsilon_\alpha \neq \varepsilon_n$. Then,

$$\langle S_{LL}^{(4)} \rangle_{non-deg} = \frac{\lambda^4}{2i\epsilon} \sum_{\alpha} \sum_{l,n} U_{\alpha l} \frac{1}{\varepsilon_{\alpha} - \varepsilon_l} U_{ln} \frac{1}{\varepsilon_{\alpha} - \varepsilon_n} \Sigma_{n\alpha}(\varepsilon_{\alpha}), \tag{64}$$

and similar terms for $\langle S_{LR}^{(4)} \rangle_{non-deg}$ and $\langle S_{RR}^{(4)} \rangle_{non-deg}$.

4 Discussion

We derived in the previous section the various terms of the S -matrix contributing to the energy shifts given by Eq. (25). It should be noted that some of them (e.g., $\langle S_{VV}^{(4)} \rangle$, $\langle S_{LV}^{(4)} \rangle_{non-deg}$ or $\langle S_{LL}^{(4)} \rangle_{non-deg}$) are of order $\mathcal{O}(1/\epsilon)$, what gives ϵ -independent energies. Others, however, have a ϵ -dependence faster than $\mathcal{O}(1/\epsilon)$; e.g., $\langle S_{LV}^{(4)} \rangle_{deg}$. These terms diverge as ϵ approaches zero. The same happens with those terms of Eq. (25) containing products, like $\langle S^{(1)} \rangle \langle S^{(3)} \rangle$. In fact, those terms cancel out the ϵ -divergences from the ones coming from $\langle S^{(4)}(1/\epsilon^n) \rangle$ such that $n > 1$. Hence, finally, we are left with energy expressions which does not diverge at the limit $\epsilon \rightarrow 0$.

In order to gain insight about the final expressions, let us discuss the energy contributions from the terms $\langle S_{VV}^{(4)} \rangle$, $\langle S_{LV}^{(4)} \rangle_{non-deg}$ and $\langle S_{LL}^{(4)} \rangle_{non-deg}$. The level shift formula Eq. (25) gives

$$\begin{aligned} \Delta E_{VV} &= -e^2 \sum_{\alpha}^{occ} \int d^3w \int d^3x \int d^3y \int d^3z \int \frac{dk_0}{2\pi i} \\ &\times \bar{\phi}_{\alpha}(\mathbf{x}) \gamma^{\mu} D_F(\mathbf{x}, \mathbf{y}; k_0) S_F(\mathbf{x}, \mathbf{w}; \varepsilon_{\alpha} - k_0) V(\mathbf{w}) \\ &\times S_F(\mathbf{w}, \mathbf{z}; \varepsilon_{\alpha} - k_0) V(\mathbf{z}) S_F(\mathbf{z}, \mathbf{y}; \varepsilon_{\alpha} - k_0) \gamma_{\mu} \phi_{\alpha}(\mathbf{y}) \end{aligned} \tag{65}$$

$$\Delta E_{LV} = \sum_{\alpha}^{occ} \sum_{\varepsilon_l \neq \varepsilon_{\alpha}} U_{\alpha l} \frac{1}{\varepsilon_{\alpha} - \varepsilon_l} \Lambda_{l\alpha}(\varepsilon_{\alpha}), \tag{66}$$

and

$$\Delta E_{LL} = \sum_{\alpha}^{occ} \sum_{l,n} U_{\alpha l} \frac{1}{\varepsilon_{\alpha} - \varepsilon_l} U_{ln} \frac{1}{\varepsilon_{\alpha} - \varepsilon_n} \Sigma_{n\alpha}(\varepsilon_{\alpha}). \tag{67}$$

The last two formulas are relatively simple and easy to interpret. ΔE_{LV} can be thought as a second order perturbation theory, written in terms of orbital energies and one-electron matrix elements, between the perturbation U and the *self-energy corrected* perturbation Λ . However, Λ can not be given in a closed form and it is only defined through its matrix elements already defined in Eq. (48). From its definition, we see that $\Lambda_{l\alpha}$ contains the external potential $V = \gamma^0 U$ such

that the whole expression ΔE_{LV} becomes quadratic in U , as we expected. Furthermore $\Lambda_{l\alpha}$ has contributions from the complete spectrum of photon frequencies k_0 .

On the other hand, the energy ΔE_{LL} shows explicitly its quadratic dependence on V , and it has a form resembling third order perturbation theory with the self-energy insertion $\Sigma_{n\alpha}$ as an additional perturbation. Both ΔE_{LV} and ΔE_{LL} are feasible to be implemented in currently existing computational codes.

Finally, the two-vertex contribution ΔE_{VV} cannot be written as a perturbation theory-like expression, showing its intrinsic QED origin. Terms like this cannot be derived from standard perturbative methods, and illustrate the usefulness of the theory presented in this work.

5 Concluding Remarks and Perspectives

We have given in this paper a theory for the inclusion of self-energy corrections to the nuclear magnetic parameters J and σ . It is based on the S -matrix formulation of bound-states quantum electrodynamics. Explicit expressions were given for first up to fourth order S -matrix terms. Divergent terms at the limit $\epsilon \rightarrow 0$ cancel out each other and ϵ -independent energy contributions are obtained. The resulting expressions have standard perturbation theory forms with new QED-derived perturbation operators added.

Some work remains to be done to get formulas computationally implementable in widely used relativistic electronic structure computational codes. Particularly, a regularization scheme must be applied in order to render our final formulas ultraviolet and infrared convergent. In previous works, dimensional regularization have proven to be effective. It should also be noted that we have not considered here other QED radiative effects like vacuum polarization, which are expected to be of the same order than those included in this work.

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