

Exchange-correlation and QED effects from a density functional based level shift approach

E. Engel^{*}, U. Lechner

Institut für Theoretische Physik, J.-W.-Goethe Universität, Frankfurt am Main, Germany

Received 24 June 2004; accepted 4 October 2004

Available online 11 November 2004

Abstract

Perturbation theory based on the auxiliary noninteracting Kohn–Sham Hamiltonian allows a systematic study of the exchange–correlation (xc) energy functional of nonrelativistic density functional theory. In particular, it serves as the starting point for the derivation of implicit (orbital-dependent) density functionals for the xc-functional. Within the framework of quantum electrodynamics, a relativistic variant of Kohn–Sham perturbation theory has been formulated in *Phys. Rev. A* 58 (1998) 964. In this approach, a coupling constant integration technique is used for the exact representation of the relativistic xc-functional.

In the present contribution an alternative systematic approach to this functional is put forward, which is based on a density functional version of Sucher’s level shift formula. As in the case of the coupling constant integration form, an exact relation for the xc-functional can be established. This relation provides the basis for a perturbation expansion to second order, including all inherent radiative corrections. A detailed comparison with the coupling constant integration result verifies the equivalence of both approaches. Finally, the first order level shift is analyzed in order to identify the Lamb shift within the Kohn–Sham scheme.

© 2004 Elsevier B.V. All rights reserved.

PACS: 31.10.+z; 31.30.Jv; 71.15.Mb

1. Introduction

Today density functional theory (DFT) is successfully applied to an enormous variety of many-particle problems. Clearly, DFT represents the method of choice for the study of particularly large or complex many-electron systems. There exists a long record of applications in condensed matter theory, ranging from early calculations for semiconductors and metals [1] to more recent work on minerals (see, e.g. [2]) and quasicrystals [3]. Similarly, the structure and dynamics of clusters [4–8], surfaces [9–11] and quantum dots [12] have been studied extensively on the basis of DFT. By now, DFT is also accepted as a standard method in quantum chemistry, as DFT results were shown to be competitive with those obtained with the more traditional quantum chemical *ab initio* techniques even for rather small molecules [13,14]. In fact, DFT proved to be useful even in atomic physics, for example for the description of atoms subject to laser fields [15] and of atomic scattering processes [16]. Moreover, the advances in computer power and the refinement of computational techniques (e.g., linear scaling) in recent years opened up yet another field for DFT applications, theoretical biophysics [17–19].

^{*} Corresponding author.

E-mail address: engel@th.physik.uni-frankfurt.de (E. Engel).

In all these areas it is routine to resort to relativistic DFT (RDFT) [20–23] whenever the nature of the system requires that (for the importance of relativity see Refs. [24,25]). For instance, a relativistic treatment has become the standard in linearized-augmented-plane-wave calculations for solids [26–28]. In the context of quantum chemistry also a number of implementations of RDFT are now available, both on the weakly relativistic [29–31] and on the fully relativistic level. In the latter case the ground state four current $j^\mu = (n, \mathbf{j}/c)$ plays the role of the density n as fundamental variable of DFT [20,23]. Unfortunately, the standard approximations for the crucial quantity of RDFT, the exchange–correlation (xc) energy functional $E_{xc}[\mathbf{j}]$, do not depend on the spatial current \mathbf{j} , as they are based on the homogeneous electron gas (in one way or another). For that reason most implementations of RDFT utilize purely density-dependent approximations for $E_{xc}[\mathbf{j}]$ [32–34], either in their standard nonrelativistic or in a relativistic form [35–38].

However, whenever magnetic moments are present this approach is inadequate. One way to circumvent this problem is to resort to the magnetization-dependent form of RDFT [23]. In this formalism the ground state magnetization density \mathbf{m} replaces the complete current \mathbf{j} . Depending on the system, either the full, noncollinear \mathbf{m} is employed or only its z -component (collinear approximation). The latter scheme represents the relativistic analog of spin-density functional theory. First applications indicate that a very accurate description of spin-polarized systems can be achieved with this approach [39–44].

An alternative route to \mathbf{j} -dependent xc-functionals is provided by the concept of implicit density functionals (for an overview see [45]). In this scheme the xc-functional is represented in terms of the Kohn–Sham (KS) single-particle orbitals, rather than explicitly in terms of n and \mathbf{j} (or \mathbf{m}). An orbital-dependent representation is most natural for the exchange energy E_x , which, within nonrelativistic DFT, is defined as the usual Fock expression evaluated with the KS orbitals [46,47]. The corresponding multiplicative potential $v_x(\mathbf{r}) = \delta E_x / \delta n(\mathbf{r})$ is obtained via the optimized potential method (OPM) [48,49]. In contrast to the standard xc-functionals, i.e. the local density approximation (LDA) and the generalized gradient approximation (GGA), the exact exchange guarantees the complete cancellation of the self-interaction in the Hartree energy, which automatically resolves some of the well-known deficiencies of the LDA and GGA (as, for instance, their inability to describe negative ions). A fully relativistic extension of this approach, including the complete transverse interaction, has been put forward recently [50].

By now, the application of the exact exchange by means of the OPM is well established in the nonrelativistic framework [51–59]. An appropriate correlation energy functional for use with the exact exchange, however, still remains to be found. Presently, the efforts towards such an E_c focus on first-principles approaches. In particular, many-body theory with the KS Hamiltonian as noninteracting reference Hamiltonian allows a systematic study of the xc-energy functional [60,61]. A perturbative evaluation of the resulting exact expression for E_c to lowest order leads to a Møller–Plesset-type functional [61], in agreement with a perturbation expansion of the celebrated adiabatic connection formula [62]. This implicit functional is the first density functional which reproduces van-der-Waals forces [59]. KS perturbation theory also forms the basis for the derivation of an RPA-type functional [63,64] and the interaction strength interpolation [65].

The question for a relativistic generalization of these concepts arises quite naturally. A fully relativistic description of atoms, molecules and solids necessarily must be based on quantum electrodynamics (QED). Within this framework, a relativistic variant of KS perturbation theory has been established in [50]. Relying on a coupling-constant integration technique, an exact expression for E_{xc} has been obtained, which, as a matter of principle, not only contains all correlation effects, but also all radiative corrections. However, the standard approach for the calculation of correlation and radiative corrections in high- Z systems is a perturbation expansion based on Sucher’s level shift formula [66–68], usually relying on the hydrogenic Hamiltonian as noninteracting reference Hamiltonian. The equivalence of these two approaches, though inevitable in principle, is not immediately obvious.

In this paper, we explicitly demonstrate this equivalence. We first formulate Sucher’s level shift within the framework of RDFT. Using the relativistic KS Hamiltonian as reference Hamiltonian the resulting level shift is essentially identical with the xc-functional (up to well-known terms). Sucher’s technique thus allows us to derive an exact relation for the relativistic E_{xc} , which represents an ideal starting point for the discussion of approximations. In particular, this relation provides the basis for a perturbation expansion, which is then used to verify the identity of the level shift with the coupling-constant integration results. In addition, it is demonstrated how the perturbation series can be simplified with the help of a relativistic form of the Sham–Schlüter equation [69]. Finally, we discuss the first order level shift in detail, in order to explicitly extract the radiative corrections, i.e. the KS Lamb shift.

The paper is organized as follows: In Section 2 a summary of the pertinent QED background is given, emphasizing the renormalization procedure required for the KS system. Section 3 outlines the essentials of RDFT. In Section 4 the level shift expression for E_{xc} is derived, which is then expanded to the order e^4 in Section 5. In Section 5 we also establish a relativistic variant of the Sham–Schlüter equation. Section 6 is devoted to a detailed discussion of the exchange energy functional. A brief summary concludes this paper. $\hbar = 1$ is used throughout.

2. Quantum electrodynamics for atomic systems

A fully relativistic description of atoms, molecules and solids necessarily must be based on quantum electrodynamics (QED). At this fundamental level the interaction between all charged particles, i.e. electrons and nuclei, is mediated by the exchange of photons. However, on the atomic energy scale, the large mass difference between electrons and nuclei allows the application of the Born–Oppenheimer approximation in its nonrelativistic form, which implies the existence of a common rest frame for all nuclei. In the electronic problem the nuclei are then treated as static external sources which can be represented either as a classical charge distribution interacting with the quantized photon field or in the form of a classical potential experienced by the quantized electron field. In this work the second of these two equivalent viewpoints is chosen. In order to keep the discussion as general as possible the static external potential representing the nuclei is assumed to be of four vector form, V^μ .

The starting point of our discussion thus is the Hamiltonian

$$\hat{H} = \hat{H}_e + \hat{H}_\gamma + \hat{H}_{\text{int}} + \hat{H}_{\text{ext}}, \quad (2.1)$$

$$\hat{H}_e = \frac{1}{2} \int d^3x [\hat{\psi}^\dagger(x), (-ic\boldsymbol{\alpha} \cdot \nabla + \beta mc^2)\hat{\psi}(x)], \quad (2.2)$$

$$\hat{H}_\gamma = -\frac{1}{8\pi} \int d^3x \{ [\partial^0 \hat{A}_\mu(x)] [\partial^0 \hat{A}^\mu(x)] + \nabla \hat{A}_\mu(x) \cdot \nabla \hat{A}^\mu(x) \}, \quad (2.3)$$

$$\hat{H}_{\text{int}} = e \int d^3x \hat{j}^\mu(x) \hat{A}_\mu(x), \quad (2.4)$$

$$\hat{H}_{\text{ext}} = e \int d^3x \hat{j}^\mu(x) V_\mu(x), \quad (2.5)$$

where $\hat{\psi}(x)$ and $\hat{A}_\mu(x)$ denote the fermion and photon field operators and $\hat{j}^\mu(x)$ is the fermion current operator,

$$\hat{j}^\mu(x) = \frac{1}{2} [\hat{\bar{\psi}}(x), \gamma^\mu \hat{\psi}(x)] \quad (2.6)$$

($\hat{\bar{\psi}} = \hat{\psi}^\dagger \gamma^0$ with the Dirac matrices γ^μ). For the photons we have chosen to work in the covariant Feynman gauge [70]. The commutator form of \hat{H}_e and \hat{j}^μ guarantees the correct behavior under charge conjugation [71]. The Hamiltonian (2.1) can be obtained from the standard Lagrangian for electrons subject to external fields [71] via Noether's theorem [70].

The ground state corresponding to (2.1) will be denoted by $|\Psi_0\rangle$,

$$\hat{H}|\Psi_0\rangle = E|\Psi_0\rangle, \quad (2.7)$$

where $|\Psi_0\rangle$ is assumed to be nondegenerate in the following.

Unfortunately, Eq. (2.7) is not well-defined without some suitable renormalization procedure. Two types of divergences have to be considered, which show up in the Green's functions of the theory as well as in expectation values for physical observables like ground state energies and four currents. The first class of divergences, the infrared divergences, is irrelevant for the present discussion and thus omitted in the following. However, the second class, the ultraviolet divergences, needs some attention.

Let us first consider a noninteracting system with the Hamiltonian

$$\hat{H}_s = \hat{H}_e + \int d^3x \hat{j}_\mu(x) v_s^\mu(x), \quad (2.8)$$

where, at this point, v_s^μ denotes some arbitrary stationary potential – the same renormalization scheme applies to all systems of type (2.8). The ground state of this system is denoted by $|\Phi_s\rangle$, the ground state energy by E_s . As it stands, the ground state expectation value $\langle \Phi_s | \hat{H}_s | \Phi_s \rangle$ diverges due to the presence of the negative energy states. This divergence is usually eliminated by explicit subtraction of the vacuum expectation value of the Hamiltonian (or, equivalently, by normal-ordering of the corresponding creation/annihilation operators).

The renormalized Hamiltonian

$$\hat{H}'_{s,R} = \hat{H}_s - \langle 0_s | \hat{H}_s | 0_s \rangle \quad (2.9)$$

with $|0_s\rangle$ representing the noninteracting vacuum in the presence of the potential v_s^μ , leads to a finite expectation value. However, with the definition (2.9) different reference energies $\langle 0_s|\hat{H}_s|0_s\rangle$ are introduced for different potentials v_s^μ . As a consequence, the comparison of ground state energies resulting from different v_s^μ is not directly possible, as the energy differences between different vacua, the so-called Casimir energy [72], are ignored. The definition (2.9) can thus not be used to establish a Hohenberg–Kohn-type existence theorem for relativistic DFT. For this purpose the ground state energy must be defined on an absolute scale, so that a unique reference energy for all external potentials is required. This can be achieved by subtracting the vacuum energy of the unperturbed vacuum $|0_0\rangle$ (obtained for $v_s^\mu = 0$), rather than $\langle 0_s|\hat{H}_s|0_s\rangle$,

$$\hat{H}_{s,R} = \hat{H}_s - \langle 0_0|\hat{H}_c|0_0\rangle. \quad (2.10)$$

The price one has to pay for this universal energy standard is the reintroduction of a divergence into the expectation values of $\hat{H}_{s,R}$. This singularity is proportional to v_s^μ and has exactly the same form as the most simple ultraviolet (UV) divergence in standard QED without external potential. The same problem exists for the ground state four current $\langle \Phi_s|\hat{j}^\mu(x)|\Phi_s\rangle$.

The origin and form of this UV divergence can be understood on the basis of a perturbative approach to the energy and current of the perturbed vacuum $|0_s\rangle$. To this aim let us consider the electron propagator of the perturbed vacuum,

$$G_{s,v}(x, y) = -i\langle 0_s|\mathbf{T}\hat{\psi}_s(x)\hat{\bar{\psi}}_s(y)|0_s\rangle,$$

where $\hat{\psi}_s(x)$ denotes the Heisenberg field operator of the system (2.8),

$$\hat{\psi}_s(x) = e^{i\hat{H}_s x^0/c}\hat{\psi}(x, x^0 = 0)e^{-i\hat{H}_s x^0/c}.$$

$G_{s,v}$ can be expressed in terms of single-particle states ϕ_k and eigenvalues ϵ_k corresponding to v_s^μ ,

$$G_{s,v}(x, y) = i\sum_k [\Theta(x^0 - y^0)(\Theta_{v,k} - 1) + \Theta(y^0 - x^0)\Theta_{v,k}]\phi_k(x)\bar{\phi}_k(y)e^{-i\epsilon_k(x^0 - y^0)/c}, \quad (2.11)$$

where $\Theta_{v,k}$ is the vacuum occupation number,

$$\Theta_{v,k} = \begin{cases} 1 & \text{for } \epsilon_k \leq -mc^2, \\ 0 & \text{for } -mc^2 < \epsilon_k. \end{cases} \quad (2.12)$$

In addition to $G_{s,v}$ one needs the propagator of QED without external potential (referred to as free QED in the following)

$$G_{0,v}(x, y) = -i\langle 0_0|\mathbf{T}\hat{\psi}_0(x)\hat{\bar{\psi}}_0(y)|0_0\rangle = \lim_{v_s^\mu \rightarrow 0} G_{s,v}(x, y). \quad (2.13)$$

With these functions one can express the energy and current of the perturbed vacuum as [73]

$$\langle 0_s|\hat{H}_{s,R}|0_s\rangle = -i\int d^3x \lim_{y \rightarrow x}^s \text{tr}[(-i\mathbf{c}\gamma \cdot \nabla + mc^2 + \gamma_\mu v_s^\mu(x))G_{s,v}(x, y)] + i\int d^3x \lim_{y \rightarrow x}^s \text{tr}[(-i\mathbf{c}\gamma \cdot \nabla + mc^2)G_{0,v}(x, y)], \quad (2.14)$$

$$\langle 0_s|\hat{j}^\mu(x)|0_s\rangle = -i\lim_{y \rightarrow x}^s \text{tr}[G_{s,v}(x, y)\gamma^\mu] \quad (2.15)$$

with the symmetric limit

$$\lim_{y \rightarrow x}^s \equiv \frac{1}{2} \left(\lim_{y \rightarrow x, y^0 > x^0} + \lim_{y \rightarrow x, y^0 < x^0} \right) \Big|_{(x-y)^2 \geq 0} \quad (2.16)$$

being a consequence of the commutator form of \hat{H}_c and \hat{j}^μ . A perturbative expansion of $G_{s,v}$ in powers of v_s^μ yields the following diagrammatic contributions,

$$G_{s,v} = \begin{array}{c} \text{---} \\ | \\ \text{---} \end{array} + \begin{array}{c} \text{---} \\ | \\ \bullet \\ | \\ \text{---} \end{array} + \begin{array}{c} \text{---} \\ | \\ \bullet \\ | \\ \text{---} \\ | \\ \bullet \\ | \\ \text{---} \end{array} + \dots \quad (2.17)$$

Here the solid line represents $G_{0,v}$, the wavy line the external potential and the dot denotes the vertex, i.e. in real space one has

$$G_{0,v,ab}(x, y) = y, b \longrightarrow x, a \quad (2.18)$$

$$v_s^\mu(\mathbf{x}) = \mathbf{x}, \mu \text{ wavy line } \times \quad (2.19)$$

$$\gamma_{ab}^\mu \delta^{(4)}(x-z) \delta^{(4)}(y-z) = \begin{array}{c} \mu \zeta z \\ \bullet \\ x \swarrow \searrow y \\ a \quad b \end{array} \quad (2.20)$$

where a, b are the spinor indices and in (2.20) x, y and z represent the coordinates of the three field operators linked at the vertex. While $G_{s,v}$ is finite as it stands, the evaluation of (2.14),(2.15) introduces one loop integration (in momentum space), for instance

$$-i \langle 0_s | \hat{j}^\mu(x) | 0_s \rangle = \text{diagram 1} + \text{diagram 2} + \text{diagram 3} + \dots \quad (2.21)$$

The fermion loops in Eq. (2.21) are identical with the standard noninteracting N -point functions of free QED: It does not make any difference whether the external potential or the quantized photon field creates virtual electron–positron pairs. As a consequence, all corresponding results of free QED apply. The renormalization procedures for $\langle 0_s | \hat{H}_{s,R} | 0_s \rangle$ and $\langle 0_s | \hat{j}^\mu(x) | 0_s \rangle$ are thus completely determined by the renormalization scheme of QED without external potential. In particular, the Furry theorem guarantees the first and third diagram in (2.21) to vanish. Only the second diagram is UV-divergent, all higher order diagrams (not displayed here) are UV finite. Moreover, the counterterm which is required for renormalization of the second diagram is a textbook matter. On the basis of dimensional regularization with space–time dimension d one finds as final counterterm for the current (2.21)

$$\Delta j^{(0),\mu}(\mathbf{x}) = -\frac{1}{12\pi^2} \Gamma\left(\frac{4-d}{2}\right) \nabla^2 v_s^\mu(\mathbf{x}), \quad (2.22)$$

where the divergence shows up as the pole of the Γ -function in the physical limit $d=4$. For the renormalized vacuum current j_v^μ one thus obtains from (2.15), (2.11) and (2.21),

$$j_v^\mu(\mathbf{x}) = \sum_k \left(\Theta_{v,k} - \frac{1}{2} \right) \phi_k^\dagger(\mathbf{x}) \alpha^\mu \phi_k(\mathbf{x}) + \Delta j^{(0),\mu}(\mathbf{x}) \quad (2.23)$$

($\alpha^\mu = \gamma^0 \gamma^\mu$). The noninteracting 2-point function is also responsible for the UV divergence of the total energy. The corresponding counterterm reads (for details see [23]),

$$\Delta E^{\text{inhom},(0)} = -\frac{1}{24\pi^2} \Gamma\left(\frac{4-d}{2}\right) \int d^3x v_{s,\mu}(\mathbf{x}) \nabla^2 v_s^\mu(\mathbf{x}). \quad (2.24)$$

It can be split into a counterterm for the external potential energy,

$$\Delta E_{\text{ext}}^{(0)} = -\frac{1}{12\pi^2} \Gamma\left(\frac{4-d}{2}\right) \int d^3x v_{s,\mu}(\mathbf{x}) \nabla^2 v_s^\mu(\mathbf{x}), \quad (2.25)$$

which makes

$$\int d^3x \langle 0_s | \hat{j}^\mu(x) | 0_s \rangle v_s^\mu(\mathbf{x}) + \Delta E_{\text{ext}}^{(0)} = \int d^3x j_v^\mu(\mathbf{x}) v_s^\mu(\mathbf{x}) \quad (2.26)$$

a finite expression, and a counterterm for the kinetic energy contribution,

$$\Delta T_s = \frac{1}{24\pi^2} \Gamma\left(\frac{4-d}{2}\right) \int d^3x v_{s,\mu}(\mathbf{x}) \nabla^2 v_s^\mu(\mathbf{x}), \quad (2.27)$$

which keeps the kinetic energy finite,

$$T_{s,v} = \sum_k \left(\Theta_{v,k} - \frac{1}{2} \right) \int d^3x \phi_k^\dagger(\mathbf{x}) [-i\mathbf{c}\boldsymbol{\alpha} \cdot \nabla + \beta mc^2] \phi_k(\mathbf{x}) - \langle 0_0 | \hat{H}_e | 0_0 \rangle + \Delta T_s, \quad (2.28)$$

$$E_{s,v} = T_{s,v} + \int d^3x j_v^\mu(\mathbf{x}) v_s^\mu(\mathbf{x}). \quad (2.29)$$

At this point all noninteracting quantities relevant for relativistic DFT are well-defined.

Let us thus now consider the interacting inhomogeneous vacuum. The basic argument which allows to identify and, at the same time, to renormalize the UV divergences of the interacting vacuum again relies on perturbation theory: As soon as a perturbation expansion of all Green's functions and relevant expectation values with respect to both the electron–electron coupling constant e^2 and the external potential V^μ is utilized, all divergent expressions correspond to the

usual divergent (sub)diagrams of QED without external potential. Their renormalization is thus uniquely determined by the standard renormalization procedure of free QED. The resulting counterterms ensure that all renormalized N -point functions of the theory are UV-finite.

Finally, the actual ground state has to be discussed. From a formal point of view this is most easily done for an extended system which approaches a homogeneous electron gas in the limit of vanishing external potential. In the case of finite systems this situation can be artificially generated by periodic repetition of the atom or molecule of interest, relying on the supercell geometry. Once the limit $V^\mu \rightarrow 0$ is well-defined, one can again apply perturbation theory with respect to both e^2 and V^μ . In this way all ground state expectation values are expressed in terms of the same diagrams as in the case of the vacuum state, with the vacuum propagator of the electrons now being replaced by the propagator of the noninteracting relativistic electron gas. One can then split any given fermion loop into its vacuum limit (obtained for vanishing gas density) and a remainder. For the vacuum part the standard prescription of free QED applies. The remainder, on the other hand, is UV finite by itself, as is clear from the power counting argument which allows the distinction of divergent and finite diagrams (see chapter 8 of [70]): The difference between the noninteracting electron gas propagator and the vacuum propagator requires an on-shell dispersion relation, so that the energy integration of the fermion loop integral breaks down, leading to a finite result. This is not only true for single loops, but also for overlapping divergences. Due to the Ward identities all diagrams of QED are exactly renormalizable, so that any propagator in a complex graph which decays faster than the free QED propagator, i.e. any break-down of an energy integration in one of the subdiagrams, makes the diagram overall superrenormalizable (of course, this does not exclude that some subdiagrams still require renormalization).

On this basis the renormalized ground state energy E and the ground state four current $j^\mu(\mathbf{x})$ can be written as

$$E = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle - \langle 0 | \hat{H}_e + \hat{H}_\gamma + \hat{H}_{\text{int}} | 0 \rangle + \Delta E, \quad (2.30)$$

$$j^\mu(\mathbf{x}) = \langle \Psi_0 | \hat{j}^\mu(\mathbf{x}) | \Psi_0 \rangle + \Delta j^\mu(\mathbf{x}), \quad (2.31)$$

where $|0\rangle$ denotes the vacuum of interacting QED without external potential, $\langle 0 | \hat{H}_e + \hat{H}_\gamma + \hat{H}_{\text{int}} | 0 \rangle$ defines the universal energy zero and ΔE and Δj^μ are the counterterms resulting from the procedure sketched above (for a more detailed discussion of ΔE and Δj^μ , see [23]).

Equations (2.30) and (2.31) together with (2.28) and (2.29) provide the solid ground for a discussion of relativistic DFT as one is now dealing with finite quantities only.

3. Basics of relativistic density functional theory

A relativistic generalization of the Hohenberg–Kohn-theorem [74] has first been put forward by Rajagopal and Callaway [20] and later by Rajagopal [21] and MacDonald and Vosko [22]. Starting from a QED-based Hamiltonian and four current, these authors demonstrated that the ground state energy is a unique functional of the ground state four current. A detailed discussion of the inherent questions of renormalization has been given in [23,75]. The two main statements of the existence theorem are:

1. There exists a one-to-one correspondence between the class of all those ground states which just differ by gauge transformations and the associated ground state four current. After the gauge has been fixed, the ground state $|\Psi_0\rangle$ is a unique functional of the four current j^μ and every ground state observable, in particular the ground state energy, can be understood as unique functional of j^μ ,

$$E[j] = \langle \Psi_0[j] | \hat{H} | \Psi_0[j] \rangle. \quad (3.1)$$

2. Minimization of $E[j]$ under the subsidiary condition of charge conservation leads to

$$\frac{\delta}{\delta j^\nu(\mathbf{x})} \{ E[j] - \mu \int d^3y j^0(\mathbf{y}) \} = 0. \quad (3.2)$$

The practical implementation of this variational principle relies on the relativistic variant [21,22] of the Kohn–Sham (KS) scheme [76]. In the following the field theoretical form of the KS scheme [23,75] is summarized.

The starting point is the assumption that there exists a noninteracting system with the same ground state four current j^μ as obtained from (2.31) for the interacting system. As this so-called KS system represents a relativistic many-particle problem, all remarks of Section 2 concerning renormalization apply. The current of the KS system thus has the form

$$j^\mu(\mathbf{x}) = \sum_k \Theta_{d,k} \phi_k^\dagger(\mathbf{x}) \alpha^\mu \phi_k(\mathbf{x}) + j_v^\mu(\mathbf{x}), \quad (3.3)$$

$$\Theta_{d,k} = \begin{cases} 0 & \text{for } \epsilon_k \leq -mc^2, \\ 1 & \text{for } -mc^2 < \epsilon_k \leq \epsilon_F, \\ 0 & \text{for } \epsilon_F < \epsilon_k \end{cases} \quad (3.4)$$

with j_v^μ given by (2.23). The total ground state energy (2.30) of the interacting system is then decomposed as

$$E = T_s + E_{\text{ext}} + E_H + E_{\text{xc}}, \quad (3.5)$$

where the individual energy components are defined as follows: T_s is the kinetic energy of the KS system,

$$T_s = \sum_k \Theta_{d,k} \int d^3x \phi_k^\dagger(\mathbf{x}) [-ic\boldsymbol{\alpha} \cdot \nabla + \beta mc^2] \phi_k(\mathbf{x}) + T_{s,v} \quad (3.6)$$

with $T_{s,v}$ given by (2.28). $E_H[j]$ represents the Hartree energy,

$$E_H[j] = \frac{1}{2} \int d^3x \int d^3y j^\mu(\mathbf{x}) D_{\mu\nu}^0(\mathbf{x} - \mathbf{y}) j^\nu(\mathbf{y}) = \frac{e^2}{2} \int d^3x \int d^3y \frac{j_\mu(\mathbf{x}) j^\mu(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} \quad (3.7)$$

defined via the noninteracting photon propagator,

$$D^{0,\mu\nu}(\mathbf{x} - \mathbf{y}) = -i \frac{e^2}{c} \langle 0_0 | \mathbf{T} \hat{A}_0^\mu(\mathbf{x}) \hat{A}_0^\nu(\mathbf{y}) | 0_0 \rangle \quad (3.8)$$

$$= \int \frac{d^4q}{(2\pi)^4} e^{-iq(\mathbf{x}-\mathbf{y})} D^{0,\mu\nu}(q) \quad (3.9)$$

$$D_{\mu\nu}^0(q) = D^0(q^2) g_{\mu\nu}, \quad D^0(q^2) = \frac{-4\pi e^2}{q^2 + i\eta} \quad (3.10)$$

(in Feynman gauge). By definition E_H contains both a Casimir contribution (E_H^{VV}) and a radiative correction (E_H^{VD}), which can be specified after insertion of (3.3) into (3.7),

$$E_H^{\text{VV}} = \frac{e^2}{2} \int d^3x \int d^3y \frac{j_{v,\mu}(\mathbf{x}) j_v^\mu(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|}, \quad (3.11)$$

$$E_H^{\text{VD}} = e^2 \int d^3x \sum_k \Theta_{d,k} \phi_k^\dagger(\mathbf{x}) \alpha_\mu \phi_k(\mathbf{x}) \int d^3y \frac{j_v^\mu(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|}. \quad (3.12)$$

In view of the expansion (2.21) for the vacuum current, E_H^{VD} is readily identified as the vacuum polarization contribution to the Lamb shift (within the present context of RDFT). The external potential term has the form

$$E_{\text{ext}}[j] = e \int d^3x j_\mu(\mathbf{x}) V^\mu(\mathbf{x}). \quad (3.13)$$

Finally, the exchange-correlation (xc) energy E_{xc} absorbs all many-body effects not contained in one of the other terms.

The variational principle (3.2) then leads to the relativistic Kohn–Sham equations

$$\{-ic\boldsymbol{\alpha} \cdot \nabla + \beta mc^2 + \alpha_\mu v_s^\mu(\mathbf{x})\} \phi_k(\mathbf{x}) = \epsilon_k \phi_k(\mathbf{x}), \quad (3.14)$$

with the multiplicative KS potential v_s^μ consisting of the sum of the nuclear potential V^μ , the Hartree potential v_H^μ and the xc-potential v_{xc}^μ ,

$$v_s^\mu(\mathbf{x}) = eV^\mu(\mathbf{x}) + v_H^\mu(\mathbf{x}) + v_{\text{xc}}^\mu(\mathbf{x}), \quad (3.15)$$

$$v_H^\mu(\mathbf{x}) = e^2 \int d^3y \frac{j^\mu(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|}, \quad (3.16)$$

$$v_{\text{xc}}^\mu(\mathbf{x}) = \frac{\delta E_{\text{xc}}[j]}{\delta j_\mu(\mathbf{x})}. \quad (3.17)$$

Eqs. (3.3), (3.14)–(3.17) have to be solved selfconsistently for given xc-functional.

4. Exchange-correlation energy: exact representation via Sucher's level shift approach

The core quantity of DFT is the xc-energy functional E_{xc} defined by Eq. (3.5). The representation chosen for E_{xc} essentially determines the many-body content of a DFT calculation and thus its predictive power. In this Section we will derive an exact expression for E_{xc} , utilizing Sucher's level shift approach [66]. As this approach represents the standard framework for QED-based perturbation theory [68,77], the resulting expression for E_{xc} is particularly helpful for the discussion of radiative effects within RDFT.

The starting point for the derivation of the level shift formula is a suitable decomposition of the interacting Hamiltonian (2.1). While in QED usually a hydrogenic Hamiltonian is employed as noninteracting reference Hamiltonian, in the context of DFT it is much more useful to work with the KS Hamiltonian, i.e. the Hamiltonian (2.8) with v_s^μ denoting the KS potential (3.15). The electron–electron interaction and the difference between v_s^μ and the actual nuclear potential V^μ are then contained in the perturbation \hat{H}_1 , for which, as usual, a dimensionless coupling constant g and an adiabatic switching function are introduced. As the adiabatic switching leads to an explicitly time-dependent Hamiltonian it is most conveniently formulated in the Schrödinger (S) representation,

$$\hat{H}_{S,\epsilon,g}(t) = \hat{H}_0 + g\hat{H}_1 e^{-\epsilon|t|} \quad (\epsilon > 0), \quad (4.1)$$

$$\hat{H}_0 = \hat{H}_s(x^0 = 0) + \hat{H}_\gamma(x^0 = 0), \quad (4.2)$$

$$\hat{H}_1 = \hat{H}_{\text{int}}(x^0 = 0) - \int d^3x \hat{j}_\mu(x^0 = 0, \mathbf{x}) \Delta v^\mu(\mathbf{x}), \quad (4.3)$$

$$\Delta v^\mu(\mathbf{x}) = v_s^\mu(\mathbf{x}) - eV^\mu(\mathbf{x}) \quad (4.4)$$

with \hat{H}_s , \hat{H}_γ and \hat{H}_{int} given by (2.8), (2.3) and (2.4), respectively. At $t = x^0/c = 0$ the Hamiltonian (4.1) agrees with the actually interesting Hamiltonian (2.1) (for $g = 1$), while for $t \rightarrow \mp\infty$ it reduces to \hat{H}_0 which represents the KS system plus noninteracting photons. Note that the expressions resulting from the decomposition (4.1) contain the standard QED scheme for $v_s^\mu(x) \rightarrow eV^\mu(x)$, as in this limit \hat{H}_0 is identical with the hydrogenic Hamiltonian (as long as one has not already used specific properties of the KS Hamiltonian).

With the decomposition (4.1) one can now go through the usual steps which lead to the Gell–Mann–Low theorem (for details see e.g., [78]). Here we only summarize the relevant definitions and results. Let us denote the time-dependent S-state corresponding to $\hat{H}_{S,\epsilon,g}(t)$ by $|\Phi_{S,\epsilon,g}(t)\rangle$,

$$i\partial_t |\Phi_{S,\epsilon,g}(t)\rangle = \hat{H}_{S,\epsilon,g}(t) |\Phi_{S,\epsilon,g}(t)\rangle. \quad (4.5)$$

As for $t \rightarrow \mp\infty$ the interaction Hamiltonian \hat{H}_1 is completely switched off, $|\Phi_{S,\epsilon,g}(t)\rangle$ approaches some S-state corresponding to \hat{H}_0 in these limits,

$$|\Phi_{S,\epsilon,g}(t)\rangle = e^{-iE_0 t} |\Phi_0\rangle \quad \text{for } t \rightarrow \mp\infty, \quad (4.6)$$

where $|\Phi_0\rangle$ is an eigenstate of \hat{H}_0 ,

$$\hat{H}_0 |\Phi_0\rangle = E_0 |\Phi_0\rangle. \quad (4.7)$$

In the following we consider the ground state, assuming that the adiabatic switching procedure preserves this state. In this case $|\Phi_0\rangle$ factorizes into the noninteracting photon vacuum $|0_\gamma\rangle$ (no free photons are present in the ground state) and the KS Slater determinant $|\Phi_s\rangle$,

$$|\Phi_0\rangle = |\Phi_s\rangle \times |0_\gamma\rangle \quad \text{with} \quad \langle 0_\gamma | \hat{A}_0^\mu(x) | 0_\gamma \rangle = 0, \quad (4.8)$$

$$|\Phi_s\rangle = \prod_{-mc^2 < \epsilon_k \leq \epsilon_F} \hat{b}_k^\dagger |0_s\rangle, \quad (4.9)$$

where \hat{b}_k^\dagger denotes the creation operator for positive energy single-particle KS states.

Accordingly, the eigenvalue E_0 is simply identical with the ground state energy of the noninteracting KS system,

$$E_0 \equiv E_s = T_s + \int d^3x j^\mu(\mathbf{x}) v_s^\mu(\mathbf{x}) \quad (4.10)$$

with T_s given by (3.6) and j^μ by (3.3). E_0 includes the vacuum energy of the KS system, explicitly specified in (2.29).

Next one introduces the interaction (I) representation with respect to the decomposition (4.1),

$$|\Phi_{I,\epsilon,g}(t)\rangle = e^{i\hat{H}_0 t} |\Phi_{S,\epsilon,g}(t)\rangle, \quad (4.11)$$

$$\hat{H}_{I,I}(t) = e^{i\hat{H}_0 t} \hat{H}_I e^{-i\hat{H}_0 t}. \quad (4.12)$$

The time-evolution of the I-picture state $|\Phi_{I,\epsilon,g}(t)\rangle$ is controlled by the I-picture time-evolution operator

$$\hat{U}_{I,\epsilon,g}(t, t') = \sum_{n=0}^{\infty} \frac{(-ig)^n}{n!} \int_{t'}^t dt_1 \cdots \int_{t'}^{t_1} dt_n e^{-\epsilon(|t_1| + \cdots + |t_n|)} \mathbf{T}[\hat{H}_{I,I}(t_1) \cdots \hat{H}_{I,I}(t_n)], \quad (4.13)$$

$$|\Phi_{I,\epsilon,g}(t)\rangle = \hat{U}_{I,\epsilon,g}(t, t') |\Phi_{I,\epsilon,g}(t')\rangle. \quad (4.14)$$

$\hat{U}_{I,\epsilon,g}(t, t')$ allows to relate the S-state of interest, $|\Phi_{S,\epsilon,g}(0)\rangle$, to the asymptotic S-state,

$$|\Phi_{S,\epsilon,g}(0)\rangle = |\Phi_{I,\epsilon,g}(0)\rangle = \lim_{t' \rightarrow \mp\infty} \hat{U}_{I,\epsilon,g}(0, t') e^{i\hat{H}_0 t'} |\Phi_{S,\epsilon,g}(t')\rangle = \hat{U}_{I,\epsilon,g}(0, \mp\infty) |\Phi_0\rangle, \quad (4.15)$$

where (4.6) has been utilized. The statement of the Gell–Mann–Low theorem applied to the present decomposition of the system then is: If

$$\lim_{\epsilon \rightarrow 0} \frac{|\Phi_{S,\epsilon,g}(0)\rangle}{\langle \Phi_0 | \Phi_{S,\epsilon,g}(0) \rangle} = \lim_{\epsilon \rightarrow 0} \frac{\hat{U}_{I,\epsilon,g}(0, \mp\infty) |\Phi_0\rangle}{\langle \Phi_0 | \hat{U}_{I,\epsilon,g}(0, \mp\infty) | \Phi_0 \rangle} \quad (4.16)$$

exists, it is an eigenstate (assumed to be nondegenerate) of the full Hamiltonian,

$$[\hat{H}_{S,\epsilon,g}(t=0) - E_g] \lim_{\epsilon \rightarrow 0} \frac{\hat{U}_{I,\epsilon,g}(0, \mp\infty) |\Phi_0\rangle}{\langle \Phi_0 | \hat{U}_{I,\epsilon,g}(0, \mp\infty) | \Phi_0 \rangle} = 0 \quad (4.17)$$

with E_g denoting the eigenvalue, i.e. the g -dependent ground state energy of the interacting system. Properly normalized to 1, the interacting ground state is given by

$$|\Phi_g\rangle = A_g \lim_{\epsilon \rightarrow 0} \frac{\hat{U}_{I,\epsilon,g}(0, \mp\infty) |\Phi_0\rangle}{\langle \Phi_0 | \hat{U}_{I,\epsilon,g}(0, \mp\infty) | \Phi_0 \rangle}, \quad (4.18)$$

$$A_g = \lim_{\epsilon \rightarrow 0} \left[\frac{\langle \Phi_0 | \hat{U}_{I,\epsilon,g}(+\infty, 0) | \Phi_0 \rangle \langle \Phi_0 | \hat{U}_{I,\epsilon,g}(0, -\infty) | \Phi_0 \rangle}{\langle \Phi_0 | \hat{U}_{I,\epsilon,g}(+\infty, -\infty) | \Phi_0 \rangle} \right]^{1/2}. \quad (4.19)$$

In the proof of the Gell–Mann–Low theorem one also verifies that

$$[\hat{H}_{S,\epsilon,g}(t=0) - E_0] \hat{U}_{I,\epsilon,g}(0, \mp\infty) |\Phi_0\rangle = \pm i\epsilon g \frac{\partial}{\partial g} \hat{U}_{I,\epsilon,g}(0, \mp\infty) |\Phi_0\rangle. \quad (4.20)$$

Multiplication of the $-$ form of (4.20) with the $+$ form of (4.16) as well as the hermitian conjugate of the $+$ form of (4.20) with the $-$ form of (4.16) finally leads to

$$E_g - E_0 = \lim_{\epsilon \rightarrow 0} \frac{i\epsilon}{2} g \frac{\partial}{\partial g} \ln \langle \Phi_0 | \hat{U}_{I,\epsilon,g}(+\infty, -\infty) | \Phi_0 \rangle. \quad (4.21)$$

Eq. (4.21) together with Eqs. (4.1)–(4.4) represents the DFT analog of Sucher's level shift formula [66] (in symmetric form).

It remains to relate the level shift (4.21) to the xc-energy functional. One first notes that the Hamiltonian of actual interest is obtained for $g = 1$. In the following this limit is thus implicitly understood whenever required (without explicit notice). With this convention Eqs. (3.5), (3.7), (3.15), (3.16), (4.10) and (4.21) yield

$$E_{xc} = \lim_{\epsilon \rightarrow 0} \frac{i\epsilon}{2} g \frac{\partial}{\partial g} \ln \langle \Phi_0 | \hat{U}_{I,\epsilon,g}(+\infty, -\infty) | \Phi_0 \rangle - E_H + \int d^3x j^\mu(\mathbf{x}) \Delta v_\mu(\mathbf{x}). \quad (4.22)$$

Eq. (4.22) provides an exact representation for E_{xc} in terms of the elements of the many-body approach defined by the decomposition (4.1). Within a perturbative picture there are three such elements. The first is the propagator of the KS system,

$$G_s(x, y) = -i \langle \Phi_s | \mathbf{T} \hat{\psi}_s(x) \hat{\bar{\psi}}_s(y) | \Phi_s \rangle, \quad (4.23)$$

$$= \int \frac{d\omega}{2\pi} e^{-i\omega(x^0 - y^0)/c} G_s(\mathbf{x}, \mathbf{y}, \omega), \quad (4.24)$$

$$G_s(\mathbf{x}, \mathbf{y}, \omega) = \sum_k \left\{ (1 - \Theta_k) \frac{\phi_k(\mathbf{x}) \bar{\phi}_k(\mathbf{y})}{\omega - \epsilon_k + i\eta} + \Theta_k \frac{\phi_k(\mathbf{x}) \bar{\phi}_k(\mathbf{y})}{\omega - \epsilon_k - i\eta} \right\} \quad (4.25)$$

with

$$\Theta_k = \Theta_{v,k} + \Theta_{d,k} \quad (4.26)$$

and ϕ_k, ϵ_k being solutions of the KS equations (3.14). The second element is the photon propagator (3.8). Finally, the Δv^μ -contribution to \hat{H}_1 , Eq. (4.3), leads to an external vertex, conceptually equivalent to some external nuclear potential. It is this last element of the many-body scheme induced by (4.1) which makes the evaluation of the crucial amplitude $\langle \Phi_0 | \hat{U}_{1,\epsilon,g}(+\infty, -\infty) | \Phi_0 \rangle$ different from the standard QED perturbation expansion. Moreover, in view of Eqs. (4.4) and (3.17) it is obvious that (4.22) is not a simple assignment, providing some well-defined expression for E_{xc} . Rather it represents a nonlinear relation for the xc-functional. Nevertheless, (4.22) allows a straightforward perturbation expansion in powers of e^2 , as will be demonstrated below.

Within the same overall framework a somewhat different exact expression for E_{xc} has been derived in [50]. The approach of [50] is based on the coupling-constant integration technique, frequently applied within DFT. The final result reads

$$E_{xc} = \frac{1}{2} \int d^4x \delta(x^0) \int d^4y D_{\mu\nu}^0(x-y) \{ \langle \Phi_0 | \mathbf{T} \hat{j}_s^\mu(x) \hat{j}_s^\nu(y) | \Phi_0 \rangle - j^\mu(\mathbf{x}) j^\nu(\mathbf{y}) \} \\ + \lim_{\epsilon \rightarrow 0} \sum_{n=1}^{\infty} \frac{(-i)^n}{(n+1)!} \int_{-\infty}^{\infty} dt_1 \cdots \int_{-\infty}^{\infty} dt_n \langle \Phi_0 | \mathbf{T} \hat{W}(0) \hat{W}(t_1) \cdots \hat{W}(t_n) | \Phi_0 \rangle_c \quad (4.27)$$

with $\hat{j}_s^\mu = [\hat{\bar{\psi}}_s, \gamma^\mu \hat{\psi}_s]/2$ and the interaction operator

$$\hat{W}(x^0) = \frac{1}{2} \int d^3x \int d^4y e^{-\epsilon(|x^0| + |y^0|)} \hat{j}_s^\mu(x) D_{\mu\nu}^0(x-y) \hat{j}_s^\nu(y) - \int d^3x e^{-\epsilon|x^0|} \hat{j}_s^\mu(x) \Delta v_\mu(\mathbf{x}). \quad (4.28)$$

In (4.27) it is implicitly understood that the time-ordering has to be established after insertion of all $\hat{W}(t_n)$, i.e. the time-ordering also applies within $\hat{W}(t_n)$. Moreover, the index c at the ground state expectation value indicates that the linked-cluster theorem has already been used to eliminate all (diagrammatic) contributions disconnected from the external vertex characterized by $\hat{W}(0)$.

While the ingredients of (4.22) and (4.27) are the same, the identity of both expressions is not immediately obvious. Clearly, within QED perturbation theory the level shift formula (4.22) is exclusively applied, while the approach (4.27) is less familiar. In the next section we will thus explicitly demonstrate that the two representations are in fact equivalent. This discussion will also show how one obtains a well-defined perturbation series from the nonlinear relation (4.22).

5. DFT level shift to second order in e^2

In this section the perturbation expansion of the level shift formula (4.22) will be considered in detail. In view of the choice for the reference Hamiltonian \hat{H}_0 and the perturbation \hat{H}_1 an expansion of the level shift in powers of e^2 is not as straightforward as in the case of the standard QED perturbation series. While the KS system is noninteracting, its particular nature implies that both the energy E_s and the potential v_s^μ depend on the electron–electron interaction. This is immediately obvious for the Hartree potential (3.16), which explicitly shows a linear dependence on the coupling-constant e^2 . As a consequence, the KS spinors ϕ_k and eigenvalues ϵ_k also depend on e^2 (by virtue of the KS equations), which, in turn, leads to an implicit dependence of v_H^μ on e^2 via j^μ . In the present situation one can thus distinguish two types of e^2 -dependences: First, there is an implicit dependence of all quantities involved, which results from the choice for \hat{H}_0 . In a perturbative framework this implicit dependence manifests itself in the propagator G_s of the reference system, which completely absorbs the dependence on ϕ_k and ϵ_k . The explicit e^2 -dependence is introduced via the photon propagator $D_{\mu\nu}^0$, which results from the perturbative treatment of the actual interaction $e \int d^3x \hat{j}^\mu \hat{A}_\mu$. Moreover, both dependences are mixed in the third element of the perturbation expansion, the ‘pseudo-external’ vertex which couples the KS system to $\Delta v^\mu = v_H^\mu + v_{xc}^\mu$.

This latter mixture can be decoupled by an expansion of E_{xc} with respect to the factor of e^2 introduced by the photon propagator,

$$E_{xc} = \sum_{i=1}^{\infty} e^{2i} \bar{E}_{xc}^{(i)} \equiv \sum_{i=1}^{\infty} E_{xc}^{(i)}, \quad (5.1)$$

which automatically induces a corresponding expansion of v_{xc}^{μ} ,

$$v_{xc}^{\mu}(\mathbf{x}) = \sum_{i=1}^{\infty} e^{2i} \bar{v}_{xc}^{\mu(i)}(\mathbf{x}) \equiv \sum_{i=1}^{\infty} v_{xc}^{\mu(i)}(\mathbf{x}). \quad (5.2)$$

$\bar{E}_{xc}^{(i)}$ and $\bar{v}_{xc}^{\mu(i)}$ still carry the full implicit e^2 -dependence via G_s . Nevertheless, insertion of (5.1) and (5.2) into (4.22) unambiguously defines a perturbation series, which is often called KS perturbation series. In the following this expansion is considered to the order e^4 .

One starts by noting that for an expansion to second order in e^2 a fourth order expansion of the amplitude $\langle \Phi_0 | \hat{U}_{I,\epsilon,g}(+\infty, -\infty) | \Phi_0 \rangle$ in powers of \hat{H}_1 is required,

$$\langle \Phi_0 | \hat{U}_{I,\epsilon,g}(+\infty, -\infty) | \Phi_0 \rangle = 1 + gU_1 + g^2U_2 + g^3U_3 + g^4U_4 + \dots \quad (5.3)$$

Insertion into (4.22) yields

$$E_{xc} = \lim_{\epsilon \rightarrow 0} \frac{i\epsilon}{2} \left\{ U_1 + 2U_2 - (U_1)^2 + 3U_3 - 3U_2U_1 + (U_1)^3 + 4U_4 - 4U_3U_1 - 2(U_2)^2 + 4U_2(U_1)^2 - (U_1)^4 + \dots \right\} - E_H + \int d^3x j^{\mu}(\mathbf{x}) \Delta v_{\mu}(\mathbf{x}).$$

The next step is the evaluation of the individual U_k . Use of (4.3) and (4.8) leads to

$$U_1 = i \int d^4x e^{-\epsilon(|x^0|)} j^{\mu}(x) \Delta v_{\mu}(x), \quad (5.5)$$

$$2U_2 - (U_1)^2 = - \int d^4x \int d^4y e^{-\epsilon(|x^0|+|y^0|)} \left[iD_{\mu\nu}^0(x-y) (j^{\mu}(\mathbf{x})j^{\nu}(\mathbf{y}) + \text{tr}[\gamma^{\mu}G_s(x,y)\gamma^{\nu}G_s(y,x)]) + \Delta v_{\mu}(\mathbf{x})\Delta v_{\nu}(\mathbf{y}) \text{tr}[\gamma^{\mu}G_s(x,y)\gamma^{\nu}G_s(y,x)] \right], \quad (5.6)$$

$$3U_3 - 3U_2U_1 + (U_1)^3 = \int d^4x \int d^4y \int d^4z e^{-\epsilon(|x^0|+|y^0|+|z^0|)} \Delta v_{\lambda}(z) \left[3D_{\mu\nu}^0(x-y) (j^{\mu}(\mathbf{x}) \text{tr}[\gamma^{\nu}G_s(y,z)\gamma^{\lambda}G_s(z,y)]) + i \text{tr}[\gamma^{\mu}G_s(x,y)\gamma^{\nu}G_s(y,z)\gamma^{\lambda}G_s(z,x)] + \Delta v_{\mu}(\mathbf{x})\Delta v_{\nu}(\mathbf{y}) \text{tr}[\gamma^{\mu}G_s(x,y)\gamma^{\nu}G_s(y,z)\gamma^{\lambda}G_s(z,x)] \right], \quad (5.7)$$

$$4U_4 - 4U_3U_1 - 2(U_2)^2 + 4U_2(U_1)^2 - (U_1)^4 = \int d^4x \int d^4y \int d^4z \int d^4u e^{-\epsilon(|x^0|+|y^0|+|z^0|+|u^0|)} \times \left\{ D_{\mu\nu}^0(x-y)D_{\lambda\rho}^0(z-u) [-2j^{\mu}(\mathbf{x})j^{\lambda}(z) \text{tr}[\gamma^{\nu}G_s(y,u)\gamma^{\rho}G_s(u,y)] - 4ij^{\mu}(\mathbf{x}) \text{tr}[\gamma^{\nu}G_s(y,z)\gamma^{\lambda}G_s(z,u)\gamma^{\rho}G_s(u,y)] - \text{tr}[\gamma^{\mu}G_s(x,z)\gamma^{\lambda}G_s(z,x)] \text{tr}[\gamma^{\nu}G_s(y,u)\gamma^{\rho}G_s(u,y)] + 2 \text{tr}[\gamma^{\mu}G_s(x,y)\gamma^{\nu}G_s(y,z)\gamma^{\lambda}G_s(z,u)\gamma^{\rho}G_s(u,x)] + \text{tr}[\gamma^{\mu}G_s(x,z)\gamma^{\lambda}G_s(z,y)\gamma^{\nu}G_s(y,u)\gamma^{\rho}G_s(u,x)] + 2iD_{\mu\nu}^0(x-y)\Delta v_{\lambda}(z)\Delta v_{\rho}(u) [+2ij^{\mu}(\mathbf{x}) \text{tr}[\gamma^{\nu}G_s(y,z)\gamma^{\lambda}G_s(z,u)\gamma^{\rho}G_s(u,y)] + \text{tr}[\gamma^{\mu}G_s(x,z)\gamma^{\lambda}G_s(z,x)] \text{tr}[\gamma^{\nu}G_s(y,u)\gamma^{\rho}G_s(u,y)] - 2 \text{tr}[\gamma^{\mu}G_s(x,y)\gamma^{\nu}G_s(y,z)\gamma^{\lambda}G_s(z,u)\gamma^{\rho}G_s(u,x)] - \text{tr}[\gamma^{\mu}G_s(x,z)\gamma^{\lambda}G_s(z,y)\gamma^{\nu}G_s(y,u)\gamma^{\rho}G_s(u,x)] - \Delta v_{\mu}(\mathbf{x})\Delta v_{\nu}(\mathbf{y})\Delta v_{\lambda}(z)\Delta v_{\rho}(u) \text{tr}[\gamma^{\mu}G_s(x,y)\gamma^{\nu}G_s(y,z)\gamma^{\lambda}G_s(z,u)\gamma^{\rho}G_s(u,x)] \right\}. \quad (5.8)$$

Taking into account Eqs. (3.15), (3.16), (4.4) and (5.2), it is obvious that the ordering of Eqs. (5.5)–(5.8) with respect to \hat{H}_1 does not directly lead to a clean powers series for E_{xc} with respect to e^2 . In order to obtain such a series Eqs. (5.5)–(5.8) have to be inserted into (5.4), followed by a reordering of the various contributions. In the same step the limit $\epsilon \rightarrow 0$ can be taken, using the effective replacement

$$\lim_{\epsilon \rightarrow 0} \epsilon e^{-\epsilon \sum_{i=1}^n |x_i^0|} \rightarrow \frac{2}{n} \delta(x_k^0), \quad (5.9)$$

where x_k^0 can be any of the n vertices of the diagram – Eq. (5.9) is explicitly verified in Appendix A. In this way one finds

$$E_{xc} = E_{xc}^{(1)} + E_{xc}^{(2)} + \mathcal{O}(e^6), \quad (5.10)$$

$$E_{xc}^{(1)} = \frac{1}{2} \int d^4x \int d^4y \delta(x^0) D_{\mu\nu}^0(x-y) \text{tr}[\gamma^\mu G_s(x,y) \gamma^\nu G_s(y,x)], \quad (5.11)$$

$$\begin{aligned} E_{xc}^{(2)} = & -\frac{i}{2} \int d^4x \int d^4y \delta(x^0) v_{xc,\mu}^{(1)}(\mathbf{x}) v_{xc,\nu}^{(1)}(\mathbf{y}) \text{tr}[\gamma^\mu G_s(x,y) \gamma^\nu G_s(y,x)] - \int d^4x \int d^4y \int d^4z \delta(z^0) v_{xc,\lambda}^{(1)}(\mathbf{z}) D_{\mu\nu}^0(x-y) \\ & \times \text{tr}[\gamma^\mu G_s(x,y) \gamma^\nu G_s(y,z) \gamma^\lambda G_s(z,x)] + \frac{i}{4} \int d^4x \int d^4y \int d^4z \int d^4u \delta(x^0) D_{\mu\nu}^0(x-y) D_{\lambda\rho}^0(z-u) \\ & \times [-\text{tr}[\gamma^\mu G_s(x,z) \gamma^\lambda G_s(z,x)] \text{tr}[\gamma^\nu G_s(y,u) \gamma^\rho G_s(u,y)] + 2\text{tr}[\gamma^\mu G_s(x,y) \gamma^\nu G_s(y,z) \gamma^\lambda G_s(z,u) \gamma^\rho G_s(u,x)] \\ & + \text{tr}[\gamma^\mu G_s(x,z) \gamma^\lambda G_s(z,y) \gamma^\nu G_s(y,u) \gamma^\rho G_s(u,x)]], \end{aligned} \quad (5.12)$$

where Eqs. (3.15), (3.16), and (4.4) have been used to eliminate all contributions containing v_H^μ . The results (5.11) and (5.12) exactly agree with the corresponding expansion of (4.27) to second order in e^2 [50]. By definition (5.11) is identified with the exact exchange of RDFT, $E_{xc}^{(1)} \equiv E_x$. $E_{xc}^{(2)}$ thus represents the lowest order correlation term.

Equation (5.12) can be slightly simplified by use of the particular nature of the reference Hamiltonian. By construction the KS system has the same ground state current as the interacting system,

$$j^\mu(\mathbf{x}) = -i \lim_{y \rightarrow x}^s \text{tr}[G(x,y) \gamma^\mu] \equiv -i \lim_{y \rightarrow x}^s \text{tr}[G_s(x,y) \gamma^\mu] \quad (5.13)$$

(the counterterms have been dropped for brevity). This fact has already been used in Eqs. (5.5)–(5.8). It can be further exploited if one expresses the interacting propagator via the reference state $|\Phi_0\rangle$ and the time-evolution operator (4.13),

$$G(x,y) = -i \frac{\langle \Phi_0 | \mathbf{T} \hat{\psi}_s(x) \bar{\psi}_s(y) \hat{U}_{I,\epsilon,g}(\infty, -\infty) | \Phi_0 \rangle}{\langle \Phi_0 | \hat{U}_{I,\epsilon,g}(\infty, -\infty) | \Phi_0 \rangle}. \quad (5.14)$$

Insertion of Eqs. (5.14) and (4.23) into (5.13) yields a relativistic extension of the Sham–Schlüter equation [69],

$$0 = \frac{\langle \Phi_0 | \mathbf{T} \hat{j}_s^\mu(x) \hat{U}_{I,\epsilon,g}(\infty, -\infty) | \Phi_0 \rangle}{\langle \Phi_0 | \hat{U}_{I,\epsilon,g}(\infty, -\infty) | \Phi_0 \rangle} - j^\mu(\mathbf{x}). \quad (5.15)$$

For the present discussion an expansion of (5.15) to second order in \hat{H}_1 is sufficient,

$$0 = j_1^\mu(\mathbf{x}) + j_2^\mu(\mathbf{x}) + \dots \quad (5.16)$$

Use of (4.13) leads to

$$j_1^\mu(\mathbf{x}) = i \int d^4z \text{tr}[\gamma^\mu G_s(x,z) \gamma^\lambda G_s(z,x)] \Delta v_\lambda(\mathbf{z}), \quad (5.17)$$

$$\begin{aligned} j_2^\mu(\mathbf{x}) = & -i \int d^4z \int d^4u \text{tr}[\gamma^\mu G_s(x,z) \gamma^\lambda G_s(z,x)] D_{\lambda\rho}^0(z-u) j^\rho(\mathbf{u}) \\ & + \int d^4z \int d^4u \text{tr}[\gamma^\mu G_s(x,z) \gamma^\lambda G_s(z,u) \gamma^\rho G_s(u,x)] \times \left(D_{\lambda\rho}^0(z-u) - i \Delta v_\lambda(\mathbf{z}) \Delta v_\rho(\mathbf{u}) \right). \end{aligned} \quad (5.18)$$

Utilizing $\Delta v^\mu = v_H^\mu + v_{xc}^\mu$ and restricting to lowest order in e^2 , Eq. (5.16) reduces to

$$i \int d^4z \text{tr}[\gamma^\mu G_s(x,z) \gamma^\lambda G_s(z,x)] v_{xc,\lambda}^{(1)}(\mathbf{z}) = - \int d^4z \int d^4u \text{tr}[\gamma^\mu G_s(x,z) \gamma^\lambda G_s(z,u) \gamma^\rho G_s(u,x)] D_{\lambda\rho}^0(z-u), \quad (5.19)$$

which is nothing but the relativistic OPM integral equation for the exact exchange potential $v_{x,\lambda} \equiv v_{xc,\lambda}^{(1)}$ [50]. Insertion of (5.19) into (5.12) finally leads to a simplified form of $E_{xc}^{(2)}$,

$$\begin{aligned} E_{xc}^{(2)} = & \frac{i}{2} \int d^4x \int d^4y \delta(x^0) v_{xc,\mu}^{(1)}(\mathbf{x}) v_{xc,\nu}^{(1)}(\mathbf{y}) \text{tr}[\gamma^\mu G_s(x,y) \gamma^\nu G_s(y,x)] + \frac{i}{4} \int d^4x \int d^4y \int d^4z \int d^4u \delta(x^0) D_{\mu\nu}^0(x-y) D_{\lambda\rho}^0(z-u) \\ & \times [-\text{tr}[\gamma^\mu G_s(x,z) \gamma^\lambda G_s(z,x)] \text{tr}[\gamma^\nu G_s(y,u) \gamma^\rho G_s(u,y)] + 2\text{tr}[\gamma^\mu G_s(x,y) \gamma^\nu G_s(y,z) \gamma^\lambda G_s(z,u) \gamma^\rho G_s(u,x)] \\ & + \text{tr}[\gamma^\mu G_s(x,z) \gamma^\lambda G_s(z,y) \gamma^\nu G_s(y,u) \gamma^\rho G_s(u,x)]]. \end{aligned} \quad (5.20)$$

It seems worthwhile to emphasize that $E_{xc}^{(2)}$ is a well-defined functional of the KS orbitals and eigenvalues, as, by definition of the power series (5.2), $v_{xc,\mu}^{(1)}$ is the functional derivative of $E_{xc}^{(1)}$,

$$v_{xc,\mu}^{(1)}(\mathbf{x}) = \frac{\delta E_{xc}^{(1)}}{\delta j^\mu(\mathbf{x})} \quad (5.21)$$

and $E_{xc}^{(1)}$ is a functional of the ϕ_k and ϵ_k only (see Eq. (5.11)). The specific expansion in powers of e^2 chosen for KS perturbation theory thus resolves the nonlinearity of the level shift formula (4.22).

6. Explicit evaluation of first order DFT level shift: exact exchange of RDFT

In this section we further evaluate the first order DFT level shift (5.11) in order to highlight its quantum electro-dynamical content. One starts by insertion of the photon propagator (3.9) and the KS propagator (4.24) into (5.11). After performing the y^0 and frequency integrations one obtains

$$E_x = \frac{e^2}{2} \int d^3x \int d^3y \int \frac{d^3q}{(2\pi)^3} e^{iq \cdot (x-y)} \frac{4\pi}{|\mathbf{q}|} \sum_{kl} \frac{\Theta_l(1 - \Theta_k)}{\omega_{kl} + |\mathbf{q}| - i\epsilon} \phi_l^\dagger(\mathbf{x}) \alpha^\mu \phi_k(\mathbf{x}) \phi_k^\dagger(\mathbf{y}) \alpha_\mu \phi_l(\mathbf{y}) \quad (6.1)$$

with

$$\omega_{kl} = (\epsilon_k - \epsilon_l)/c. \quad (6.2)$$

It seems worthwhile to emphasize that the frequency integrations which lead to the expression (6.1) are well-defined even if the photon propagator is replaced by the instantaneous Coulomb interaction, i.e. if both the q^0 -dependence and the spatial components of $g^{\mu\nu}$ are dropped in $D_{\mu\nu}^0(q)$, Eq. (3.10). In this Coulomb limit Eq. (6.1) is obtained with $\omega_{kl} = 0$ and α^μ replaced by $\alpha^0 = 1$. However, as it stands the expression (6.1) with these replacements diverges,

$$E_x^C = -\frac{e^2}{2} \int d^3x \int d^3y \int \frac{d^3q}{(2\pi)^3} e^{iq \cdot (x-y)} \frac{4\pi}{|\mathbf{q}|^2} \times \left\{ \sum_{kl} \Theta_k \Theta_l \phi_l^\dagger(\mathbf{x}) \phi_k(\mathbf{x}) \phi_k^\dagger(\mathbf{y}) \phi_l(\mathbf{y}) - \sum_l \Theta_l \phi_l^\dagger(\mathbf{x}) \phi_l(\mathbf{y}) \delta^{(3)}(\mathbf{x} - \mathbf{y}) \right\} \quad (6.3)$$

(the completeness of the ϕ_k has been used in the last term). This divergence reflects the operator ordering in the interaction Hamiltonian: While QED inevitably leads to a $\hat{j}^\mu(x)\hat{j}^\nu(y)$ -type interaction between two vertices x and y , nonrelativistic many-body theory with its instantaneous interaction already starts with a properly ordered $\hat{\psi}^\dagger(x)\hat{\psi}^\dagger(y)\hat{\psi}(y)\hat{\psi}(x)$ -type Hamiltonian. As a consequence, self-interaction terms as the divergent contribution to (6.3) are avoided from the very outset. In a field theoretical framework, on the other hand, the elimination of these terms is the task of the renormalization scheme.

In order to discuss E_x in more detail it is most convenient to decompose (6.1) by use of (4.26),

$$E_x = E_x^{VV} + E_x^{VD} + E_x^{DD}, \quad (6.4)$$

$$E_x^{VV} = e^2 \int d^3x \int d^3y \int_0^\infty \frac{dq}{\pi} \frac{\sin(q|\mathbf{x} - \mathbf{y}|)}{|\mathbf{x} - \mathbf{y}|} \sum_{kl} \Theta_{v,l}(1 - \Theta_{v,k}) \frac{\phi_l^\dagger(\mathbf{x}) \alpha^\mu \phi_k(\mathbf{x}) \phi_k^\dagger(\mathbf{y}) \alpha_\mu \phi_l(\mathbf{y})}{\omega_{kl} + q - i\epsilon}, \quad (6.5)$$

$$E_x^{VD} = e^2 \Re \int d^3x \int d^3y \int_0^\infty \frac{dq}{\pi} \frac{\sin(q|\mathbf{x} - \mathbf{y}|)}{|\mathbf{x} - \mathbf{y}|} \sum_{kl} \Theta_{d,l} \left\{ \frac{1 - \Theta_{v,k}}{\omega_{kl} + q - i\epsilon} + \frac{\Theta_{v,k}}{\omega_{kl} - q + i\epsilon} \right\} \times \phi_l^\dagger(\mathbf{x}) \alpha^\mu \phi_k(\mathbf{x}) \phi_k^\dagger(\mathbf{y}) \alpha_\mu \phi_l(\mathbf{y}), \quad (6.6)$$

$$E_x^{DD} = -\frac{e^2}{2} \int d^3x \int d^3y \sum_{kl} \Theta_{d,k} \Theta_{d,l} \frac{\cos[\omega_{kl}|\mathbf{x} - \mathbf{y}|]}{|\mathbf{x} - \mathbf{y}|} \phi_l^\dagger(\mathbf{x}) \alpha^\mu \phi_k(\mathbf{x}) \phi_k^\dagger(\mathbf{y}) \alpha_\mu \phi_l(\mathbf{y}). \quad (6.7)$$

In the last contribution, the exchange energy of the occupied discrete KS states, the integration over q has been performed in order to obtain a more familiar form. Using

$$\int_0^\infty dq \frac{\sin(q|\mathbf{x}|)}{\omega + q - i\epsilon} = \text{ci}(\omega|\mathbf{x}|) \sin(\omega|\mathbf{x}|) - \text{si}(\omega|\mathbf{x}|) \cos(\omega|\mathbf{x}|) \quad (6.8)$$

analogous expressions can be given for the other two terms. The decomposition (6.4) can also be obtained from a splitting of the two KS propagators (4.25) in (5.11) into their vacuum limit (2.11) and a remainder comprising the occupied discrete KS levels

Fock orbitals, the KS orbitals thus yield a gauge invariant E_x^{DD} . The more familiar Coulomb and Breit exchange can be obtained from (6.7) by expansion of $\cos[\omega_{kl}|\mathbf{x} - \mathbf{y}|]$ in powers of $1/c^2$ and subsequent use of the KS equation (in order to eliminate ϵ_k in favor of the operator $\boldsymbol{\alpha} \cdot \nabla$).

7. Concluding remarks

With the level shift formula (4.22) an exact representation of the xc-energy functional of RDFT is available which is formulated on equal footing with the standard QED perturbation series. The level shift expression is an implicit density functional, as it depends on the KS orbitals and eigenvalues. As such its self-consistent application requires the solution of the relativistic OPM integral equation [50]. While this solution is straightforward for the no-pair exchange, the interplay between vacuum corrections and the OPM integral equation remains to be investigated. In particular, it is not clear whether the required summations over positive and negative energy continuum states lead to similar problems as the summation over unoccupied KS states in the case of the nonrelativistic correlation functional [79]. In any case, the inclusion of the appropriate counterterms in the integral equation represents a serious technical problem.

On the other hand, a perturbative evaluation of radiative corrections within the framework of RDFT could directly start from the expressions provided in Sections 5 and 6. In fact, one could hope that the implicit partial resummation of the QED perturbation series inherent in the KS reference Hamiltonian leads to an improved convergence as compared to the standard procedure starting from a hydrogenic reference Hamiltonian.

In the present work the (unknown) exact KS Hamiltonian has been employed as noninteracting reference Hamiltonian. Clearly, the many-body approach chosen can equally well be based on some approximate KS Hamiltonian, for instance resulting from a (no-pair) LDA or an exchange-only calculation. In this case, however, all relations specific to the exact KS Hamiltonian, as the identity of the KS current with the interacting current and thus the relativistic Sham–Schlüter equation, can no longer be used to simplify the perturbation series.

Although not pursued here, it is obvious that the level shift formula can also be utilized for a partial resummation of the KS series. Such a resummation is only of limited interest in the context of radiative corrections, but could be quite useful for the construction of approximate relativistic xc-functionals. In this case efficiency requires the level shift formula to be exploited within the no-(virtual)-pair approximation. While the no-pair approximation can only be defined for given noninteracting reference Hamiltonian and thus depends on the approximation for E_{xc} one finally comes up with, this subtlety is not expected to play a role in standard electronic structure calculations.

Acknowledgment

Financial support by the Deutsche Forschungsgemeinschaft (Project EN 265/4-1) is gratefully acknowledged.

Appendix A. Time integration

In this appendix the time integration involved in the level shift formula (4.22) is analyzed in some detail. In particular, this analysis addresses the interrelation of the time integration with the limit $\epsilon \rightarrow 0$.

Let us first consider a single vertex. At each interaction vertex the time integration has the structure

$$W_i = \int_{-\infty}^{+\infty} dx_i^0 e^{-\epsilon|x_i^0|} D_{\mu\nu}^0(x_i - x_j) G_s(x_k, x_i) \gamma^\mu G_s(x_i, x_l), \quad (\text{A.1})$$

where x_j , x_k and x_l represent the neighboring vertices (on which no information is required at this point). W_i can be evaluated by use of the Lehmann representation for G_s , Eq. (4.24), and $D_{\mu\nu}$, Eq. (3.9),

$$\begin{aligned} W_i &= \int_{-\infty}^{+\infty} dx_i^0 e^{-\epsilon|x_i^0|} \int \frac{dq^0}{2\pi} e^{-iq^0(x_i^0 - x_j^0)} \int \frac{d\omega_1}{2\pi} e^{-i\omega_1(x_k^0 - x_i^0)} \int \frac{d\omega_2}{2\pi} e^{-i\omega_2(x_i^0 - x_l^0)} D_{\mu\nu}^0(\mathbf{x}_i - \mathbf{x}_j, q^0) G_s(\mathbf{x}_k, \mathbf{x}_i, \omega_1) \gamma^\mu G_s(\mathbf{x}_i, \mathbf{x}_l, \omega_2), \\ &= \int \frac{dq^0}{2\pi} e^{iq^0 x_j^0} \int \frac{d\omega_1}{2\pi} e^{-i\omega_1 x_k^0} \int \frac{d\omega_2}{2\pi} e^{i\omega_2 x_l^0} \left[\frac{1}{\epsilon + i(q^0 - \omega_1 + \omega_2)} + \frac{1}{\epsilon - i(q^0 - \omega_1 + \omega_2)} \right] \\ &\quad \times D_{\mu\nu}^0(\mathbf{x}_i - \mathbf{x}_j, q^0) G_s(\mathbf{x}_k, \mathbf{x}_i, \omega_1) \gamma^\mu G_s(\mathbf{x}_i, \mathbf{x}_l, \omega_2). \end{aligned}$$

In the limit $\epsilon \rightarrow 0$ the Dirac identity can then be used to obtain

$$W_i = \int \frac{dq^0}{2\pi} e^{-iq^0(x_i^0 - x_j^0)} \int \frac{d\omega}{2\pi} e^{-i\omega(x_k^0 - x_l^0)} D_{\mu\nu}^0(\mathbf{x}_i - \mathbf{x}_j, q^0) G_s(\mathbf{x}_k, \mathbf{x}_i, \omega) \gamma^\mu G_s(\mathbf{x}_i, \mathbf{x}_l, \omega - q^0). \quad (\text{A.2})$$

The situation is even more simple for a vertex with the external potential,

$$V_i = \int_{-\infty}^{+\infty} dx_i^0 e^{-\epsilon|x_i^0|} \Delta v_\mu(\mathbf{x}_i) G_s(\mathbf{x}_k, \mathbf{x}_i) \gamma^\mu G_s(\mathbf{x}_i, \mathbf{x}_l) = \int \frac{d\omega}{2\pi} e^{-i\omega(x_k^0 - x_l^0)} \Delta v_\mu(\mathbf{x}_i) G_s(\mathbf{x}_k, \mathbf{x}_i, \omega) \gamma^\mu G_s(\mathbf{x}_i, \mathbf{x}_l, \omega). \quad (\text{A.3})$$

The first point to note thus is that at each individual vertex of a given contribution to (4.22) the limit $\epsilon \rightarrow 0$ could be taken before integration over the corresponding time coordinate. The result is a δ -function in frequency space for both orderings of limit and integration.

Let us now turn to a complete diagram resulting from (4.22). It consists of an even number of $2n$ interaction vertices, connected by $2n$ dressed KS propagators and n photon propagators D^0 . Each dressed KS propagator consists of k simple KS propagators G_s and $k-1$ external vertices Δv_μ . However, Eq. (A.3) demonstrates that the structure of these products of G_s and Δv_μ with respect to time is the same as that of a single G_s . In the following the discussion can thus be restricted to diagrams which do not contain any external vertex without loss of generality.

The time integration of such a diagram has the general form

$$I_\epsilon^{2n} = \prod_{i=1}^{2n} \int_{-\infty}^{\infty} dx_i^0 e^{-\epsilon|x_i^0|} \prod_{k=1}^{2n} \int \frac{d\omega_k}{2\pi} e^{-i\omega_k(x_k^0 - x_{P(k)}^0)} \prod_{l=1}^n \int \frac{dq_l^0}{2\pi} e^{-iq_l^0(x_l^0 - x_{P'(n+l)}^0)} F(\omega_1, \dots, \omega_{2n}, q_1^0, \dots, q_n^0), \quad (\text{A.4})$$

with P and P' denoting permutations of the time variables. P and P' are characteristic for the diagram under consideration. If one could take the limit $\epsilon \rightarrow 0$ in this expression rightaway, the integrations over the time variables would directly lead to δ -functions in frequency space. However, for $\epsilon = 0$ the integrand of (A.4) only depends on time differences, rather than the absolute times x_k^0 . Consequently, after $2n-1$ of the integrations have been performed the resulting expression does no longer depend on the remaining $2n$ -th time variable (by virtue of the relations between the ω_k and q_l^0 enforced by the $2n-1$ δ -functions obtained from the first $2n-1$ integrations). The final time integral thus diverges, if $\epsilon \rightarrow 0$ is applied before performing any of the time integrations.

On the other hand, I_ϵ^{2n} is multiplied by an overall prefactor of ϵ in Eq. (4.22), so that only the product ϵI_ϵ^{2n} has to exist for $\epsilon \rightarrow 0$. Obviously, the limit $\epsilon \rightarrow 0$ can not be interchanged with the time integrations.

Let us thus consider I_ϵ^{2n} for $\epsilon > 0$. In order to evaluate (A.4) one chooses one of the x_k^0 , say x_1^0 , to rescale all remaining times,

$$\tau_i = x_1^0 - x_i^0, \quad i = 1, \dots, 2n. \quad (\text{A.5})$$

As a consequence, the variable x_1^0 does no longer occur in the Fourier exponentials of the propagators,

$$\begin{aligned} I_\epsilon^{2n} &= \int_{-\infty}^{\infty} dx_1^0 \prod_{i=2}^{2n} \int_{-\infty}^{\infty} d\tau_i e^{-\epsilon \sum_{j=1}^{2n} |x_1^0 - \tau_j|} \prod_{k=1}^{2n} \int \frac{d\omega_k}{2\pi} e^{-i\omega_k(\tau_k - \tau_{P(k)})} \prod_{l=1}^n \int \frac{dq_l^0}{2\pi} e^{-iq_l^0(\tau_l - \tau_{P'(n+l)})} F(\omega_1, \dots, \omega_{2n}, q_1^0, \dots, q_n^0) \\ &= \prod_{i=1}^{2n} \int_{-\infty}^{\infty} d\tau_i \delta(\tau_i) \prod_{k=1}^{2n} \int \frac{d\omega_k}{2\pi} e^{-i\omega_k(\tau_k - \tau_{P(k)})} \\ &\quad \times \prod_{l=1}^n \int \frac{dq_l^0}{2\pi} e^{-iq_l^0(\tau_l - \tau_{P'(n+l)})} F(\omega_1, \dots, \omega_{2n}, q_1^0, \dots, q_n^0) \int_{-\infty}^{\infty} dx_1^0 e^{-\epsilon \sum_{j=1}^{2n} |x_1^0 - \tau_j|}. \end{aligned} \quad (\text{A.6})$$

The crucial integral to be examined in the following is the x_1^0 -integral of the last line.

Let t_i be that permutation of the τ_i for which

$$t_i \leq t_{i+1} \quad \forall i. \quad (\text{A.7})$$

Then evaluate

$$J_\epsilon^{2n} = \int_{-\infty}^{\infty} dx e^{-\epsilon \sum_{i=1}^{2n} |x-\tau_i|} \equiv \int_{-\infty}^{\infty} dx e^{-\epsilon \sum_{i=1}^{2n} |x-t_i|}, \quad (\text{A.8})$$

$$\begin{aligned} &= \lim_{t_0 \rightarrow -\infty} \lim_{t_{2n+1} \rightarrow \infty} \sum_{j=1}^{2n+1} \int_{t_{j-1}}^{t_j} dx e^{-\epsilon \sum_{i=1}^{j-1} (x-t_i)} e^{-\epsilon \sum_{i=j}^{2n} (t_i-x)}, \\ &= \lim_{t_0 \rightarrow -\infty} \lim_{t_{2n+1} \rightarrow \infty} \sum_{j=1, j \neq n+1}^{2n+1} \frac{1}{2\epsilon(n-j+1)} \left\{ e^{-\epsilon \sum_{i=1}^{2n} |t_i-t_j|} - e^{-\epsilon \sum_{i=1}^{2n} |t_i-t_{j-1}|} \right\} \\ &\quad + e^{-\epsilon \sum_{i=1}^n (t_{n+i}-t_i)} (t_{n+1} - t_n), \\ &= \sum_{j=1, j \neq n+1}^{2n} \frac{1}{2\epsilon(n-j+1)} e^{-\epsilon \sum_{i=1}^{2n} |t_i-t_j|} - \sum_{j=2, j \neq n+1}^{2n+1} \frac{1}{2\epsilon(n-j+1)} e^{-\epsilon \sum_{i=1}^{2n} |t_i-t_{j-1}|} \\ &\quad + t_{n+1} e^{-\epsilon \sum_{i=1}^{2n} |t_i-t_{n+1}|} - t_n e^{-\epsilon \sum_{i=1}^{2n} |t_i-t_n|}. \end{aligned} \quad (\text{A.9})$$

Equation (A.9) clearly exhibits the divergence of the $2n$ th time integration. Nevertheless, after the first time integration has been performed the appropriate limit $\epsilon \rightarrow 0$ is well-defined,

$$\lim_{\epsilon \rightarrow 0} \epsilon J_\epsilon^{2n} = \frac{2}{(2n)}. \quad (\text{A.10})$$

An analogous result is obtained for an odd number of time variables (i.e., vertices), so that one has quite generally

$$\lim_{\epsilon \rightarrow 0} \epsilon J_\epsilon^n = \frac{2}{n}. \quad (\text{A.11})$$

One can finally use this result in Eq. (A.6) and transform back all time variables to their initial form,

$$x_1^0 = \tau_1 \quad x_i^0 = \tau_1 - \tau_i \quad i = 2, \dots, 2n \quad (\text{A.12})$$

to obtain

$$\begin{aligned} \lim_{\epsilon \rightarrow 0} \epsilon I_\epsilon^{2n} &= \frac{2}{(2n)} \prod_{i=1}^{2n} \int_{-\infty}^{\infty} dx_i^0 \delta(x_1^0) \prod_{k=1}^{2n} \int \frac{d\omega_k}{2\pi} e^{-i\omega_k(x_k^0 - x_{P(k)}^0)} \\ &\quad \times \prod_{l=1}^n \int \frac{dq_l^0}{2\pi} e^{-iq_l^0(x_l^0 - x_{P'(n+l)}^0)} F(\omega_1, \dots, \omega_{2n}, q_1^0, \dots, q_n^0). \end{aligned} \quad (\text{A.13})$$

For an arbitrary Feynman diagram with n vertices (n th order in \hat{H}_1) one thus finds the effective replacement (5.9).

References

- [1] P.M. Marcus, J.F. Janak, A.R. Williams (Eds.), Computational Methods in Band Theory, Plenum, New York, 1971.
- [2] C.J. Pickard, B. Winkler, R.K. Chen, M.C. Payne, M.H. Lee, J.S. Lin, J.A. White, V. Milman, D. Vanderbilt, Phys. Rev. Lett. 85 (2000) 5122.
- [3] M. Krajci, J. Hafner, M. Mihalkovic, Phys. Rev. B 56 (1997) 3072.
- [4] R.N. Barnett, U. Landman, Phys. Rev. B 48 (1993) 2081.
- [5] W. Andreoni, Annual Rev. Phys. Chem. 49 (1998) 405.
- [6] G.F. Bertsch, A. Bulgac, D. Tomanek, Y. Wang, Phys. Rev. Lett. 67 (1991) 2690.
- [7] F.S. Zhang, F. Spiegelmann, E. Suraud, V. Fraysse, R. Poteau, R. Glowinski, F. Chatelin, Phys. Lett. A 193 (1994) 75.
- [8] F. Rohmund, E.E.B. Campbell, O. Knospe, G. Seifert, R. Schmidt, Phys. Rev. Lett. 76 (1996) 3289.
- [9] S. Blonski, S.H. Garofalini, J. Chem. Phys. 100 (1995) 2201.
- [10] C.G. Morgan, P. Kratzer, M. Scheffler, Phys. Rev. Lett. 82 (1999) 4886.
- [11] M. Petersen, S. Wilke, P. Ruggerone, B. Kohler, M. Scheffler, Phys. Rev. Lett. 76 (1996) 995.
- [12] S.M. Reimann, M. Manninen, Rev. Mod. Phys. 74 (2002) 1283.
- [13] A. Becke, J. Chem. Phys. 96 (1992) 2155.
- [14] B.G. Johnson, P.M. Gill, J.A. Pople, J. Chem. Phys. 98 (1993) 5612.
- [15] C.A. Ullrich, E.K.U. Gross, Comm. At. Molec. Phys. 33 (1997) 211.
- [16] T. Kirchner, L. Gulyas, H.-J. Lüdde, A. Henne, E. Engel, R.M. Dreizler, Phys. Rev. Lett. 79 (1997) 1658.
- [17] S. Sirois, E.I. Proynov, D.T. Nguyen, D.R. Salahub, J. Chem. Phys. 107 (1997) 6770.

- [18] M. Benoit, D. Marx, M. Parrinello, *Nature* 392 (1998) 258.
- [19] M. Eichinger, P. Tavan, J. Hutter, M. Parrinello, *J. Chem. Phys.* 110 (1999) 10452.
- [20] A.K. Rajagopal, J. Callaway, *Phys. Rev. B* 7 (1973) 1912.
- [21] A.K. Rajagopal, *J. Phys. C* 11 (1978) L943.
- [22] A.H. MacDonald, S.H. Vosko, *J. Phys. C* 12 (1979) 2977.
- [23] E. Engel, in: P. Schwerdtfeger (Ed.), *Relativistic Electronic Structure Theory, Part I. Fundamentals*, Elsevier, Amsterdam, 2002, p. 524.
- [24] P. Pyykkö, *Chem. Rev.* 88 (1988) 563.
- [25] M. Pepper, B.E. Bursten, *Chem. Rev.* 91 (1991) 719.
- [26] A.H. MacDonald, J.M. Daams, S.H. Vosko, D.D. Koelling, *Phys. Rev. B* 23 (1981) 6377.
- [27] A.H. MacDonald, J.M. Daams, S.H. Vosko, D.D. Koelling, *Phys. Rev. B* 25 (1982) 713.
- [28] P. Blaha, K. Schwarz, P. Dufek, R. Augustyn, wIEN95, Technical University of Vienna, 1995. (Improved and updated Unix version of the original copyrighted WIEN-code, by P. Blaha, K. Schwarz, P. Sorantin, S.B. Trickey, *Comput. Phys. Commun.* 59 (1990) 399).
- [29] E.J.B., et al., *Chem. Phys.* 2 (1973) 41, aDF 2.3.0, Theoretical Chemistry, Vrije Universiteit, Amsterdam.
- [30] E. van Lente, E.J. Baerends, J.G. Snijders, *J. Chem. Phys.* 101 (1994) 1272.
- [31] M. Mayer, O.D. Haberen, N. Rosch, *Phys. Rev. A* 54 (1996) 4775.
- [32] A. Rosen, D.E. Ellis, *J. Chem. Phys.* 62 (1975) 3039.
- [33] S. Varga, E. Engel, W.-D. Sepp, B. Fricke, *Phys. Rev. A* 59 (1999).
- [34] W. Liu, C. van Wüllen, *J. Chem. Phys.* 110 (1999) 3730.
- [35] I.A. Akhiezer, S.V. Peletminskii, *Zh. Eksp. Teor. Fiz.* 38 (1960) 1829, [*Sov. Phys. JETP* 11 (1960) 1316].
- [36] M.V. Ramana, A.K. Rajagopal, *Phys. Rev. A* 24 (1981) 1689.
- [37] E. Engel, S. Keller, R.M. Dreizler, *Phys. Rev. A* 53 (1996) 1367.
- [38] R.N. Schmid, E. Engel, R.M. Dreizler, P. Blaha, K. Schwarz, *Adv. Quant. Chem.* 33 (1998) 209.
- [39] L. Nordstrom, D.J. Singh, *Phys. Rev. Lett.* 76 (1996) 4420.
- [40] L.M. Sandratskii, *Adv. Phys.* 47 (1998) 91.
- [41] H. Eschrig, V.D.P. Servedio, *J. Comput. Chem.* 20 (1999) 23.
- [42] J. Anton, T. Jacob, B. Fricke, E. Engel, *Phys. Rev. Lett.* 89 (2002) 213001.
- [43] J. Anton, B. Fricke, E. Engel, *Phys. Rev. A* 69 (2004) 012505.
- [44] F. Wang, W.J. Liu, *J. Chin. Chem. Soc. (Taipei)* 50 (2003) 597.
- [45] E. Engel, in: C. Fiolhais, M. Marques, F. Nogueira (Eds.), *Density Functional Theory*, Springer, Berlin, 2003, p. 56.
- [46] V. Sahni, J. Gruenebaum, J.P. Perdew, *Phys. Rev. B* 26 (1982) 4371.
- [47] D.C. Langreth, M.J. Mehl, *Phys. Rev. B* 28 (1983) 1809.
- [48] R.T. Sharp, G.K. Horton, *Phys. Rev.* 90 (1953) 317.
- [49] J.D. Talman, W.F. Shadwick, *Phys. Rev. A* 14 (1976) 36.
- [50] E. Engel, A. Facco Bonetti, S. Keller, I. Andrejkovics, R.M. Dreizler, *Phys. Rev. A* 58 (1998) 964.
- [51] J.B. Krieger, Y. Li, G.J. Iafrate, *Phys. Lett. A* 146 (1990) 256.
- [52] E. Engel, S.H. Vosko, *Phys. Rev. A* 47 (1993) 2800.
- [53] T. Kotani, *Phys. Rev. B* 50 (1994) 14816.
- [54] D.M. Bylander, L. Kleinman, *Phys. Rev. Lett.* 74 (1995) 3660.
- [55] T. Grabo, E.K.U. Gross, *Chem. Phys. Lett.* 240 (1995) 141.
- [56] M. Städele, J.A. Majewski, P. Vogl, A. Gorling, *Phys. Rev. Lett.* 79 (1997) 2089.
- [57] A. Gorling, *Phys. Rev. Lett.* 83 (1999) 5459.
- [58] S. Ivanov, S. Hirata, R.J. Bartlett, *Phys. Rev. Lett.* 83 (1999) 5455.
- [59] E. Engel, A. Höck, R.M. Dreizler, *Phys. Rev. A* 61 (2000) 032502.
- [60] L.J. Sham, *Phys. Rev. B* 32 (1985) 3876.
- [61] E. Engel, R.M. Dreizler, *J. Comput. Chem.* 20 (1999) 31.
- [62] A. Görling, M. Levy, *Phys. Rev. A* 50 (1994) 196.
- [63] T. Kotani, *J. Phys.: Condens. Matter* 10 (1998) 9241.
- [64] E. Engel, A. Facco Bonetti, in: A. Hernandez-Laguna, J. Maruani, R. McWeeny, S. Wilson (Eds.), *Quantum Systems in Theoretical Chemistry and Physics, Basic Problems and Model Systems*, vol. 1, Kluwer, Dordrecht, 2000, p. 227.
- [65] M. Seidl, J.P. Perdew, S. Kurth, *Phys. Rev. Lett.* 84 (2000) 5070.
- [66] J. Sucher, *Phys. Rev.* 107 (1957) 1448.
- [67] P.J. Mohr, in: W.R. Johnson, P.J. Mohr, J. Sucher (Eds.), *Relativistic, Quantum Electrodynamics and Weak Interaction Effects in Atoms*, AIP, New York, 1989, p. 47.
- [68] J. Sapirstein, *Rev. Mod. Phys.* 70 (1998) 55.
- [69] L.J. Sham, M. Schlüter, *Phys. Rev. Lett.* 51 (1983) 1888.
- [70] C. Itzykson, J.-B. Zuber, *Quantum Field Theory*, McGraw-Hill, New York, 1980.
- [71] A.O.G. Källén, *Handbuch der Physik, Band V, Teil 1*, Springer, Berlin, 1958.
- [72] G. Plunien, B. Müller, W. Greiner, *Phys. Rep.* 134 (1986) 87.
- [73] W. Greiner, B. Müller, J. Rafelski, *Quantum Electrodynamics of Strong Fields*, Springer, Berlin, 1985.
- [74] P. Hohenberg, W. Kohn, *Phys. Rev. B* 136 (1964) 864.
- [75] E. Engel, H. Müller, C. Speicher, R.M. Dreizler, in: E.K.U. Gross, R.M. Dreizler (Eds.), *Density Functional Theory*, NATO ASI Series B, vol. 337, Plenum, New York, 1995, p. 65.
- [76] W. Kohn, L.J. Sham, *Phys. Rev. A* 140 (1965) 1133.
- [77] P.J. Mohr, *Phys. Rev. A* 32 (1985) 1949.
- [78] A.L. Fetter, J.D. Walecka, *Quantum Theory of Many-Particle Systems*, McGraw-Hill, New York, 1971.
- [79] A. Facco Bonetti, E. Engel, R.N. Schmid, R.M. Dreizler, *Phys. Rev. Lett.* 86 (2001) 2241.