Appendix A
Functionals and the Functional Derivative

In this Appendix we provide a minimal introduction to the concept of functionals and the functional derivative. No attempt is made to maintain mathematical rigor. A more extended and mathematically more precise discussion of the material summarized here can be found in the books of Courant and Hilbert [728] and of Atkinson and Han [29] (for the special context of DFT see also [28]).

A.1 Definition of the Functional

A functional is defined by a rule, which associates a number (real or complex) with a function of one or several variables,

$$f(x) \text{ or } f(\boldsymbol{r}_1, \ldots) \quad \xrightarrow{\text{rule}} \quad F[f] \,, \tag{A.1}$$

or, more generally, which associates a number with a set of functions,

$$f_1, f_2, \ldots \quad \xrightarrow{\text{rule}} \quad F[f_1, f_2, \ldots] \,. \tag{A.2}$$

This definition is quite well described by the designation as a function of a function. Some examples are:

- A definite integral over a continuous function $f(x)$

$$F[f] = \int_{x_1}^{x_2} f(x) dx \tag{A.3}$$

  (similarly one can have integrals with functions of several variables).
- A slightly more general form is

$$F_w[f] = \int_{x_1}^{x_2} w(x) f(x) dx \,, \tag{A.4}$$

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that is an integral over the function f with a fixed weight function $w(x)$.

- A prescription which associates a function with the value of this function at a particular point in the interior of a given interval $[x_1, x_2]$

$$F[f] = f(x_0) \qquad x_0 \in (x_1, x_2)\,. \tag{A.5}$$

This functional can be represented in integral form with the aid of the δ-function,

$$F_\delta[f] = \int_{x_1}^{x_2} \delta(x - x_0) f(x) dx\,, \tag{A.6}$$

that is with a weight function in the form of a generalized function (a distribution).

The examples (A.3) and (A.5) directly show that a functional can itself be a function of a variable, i.e. of one of the parameters in its definition, as the boundaries in the integral (A.3) or the point x_0 in the functional (A.5). The dependence on such a parameter y is denoted as $F[f](y)$.

So far, all examples are characterized by the fact that they depend linearly on the function $f(x)$, so that they satisfy the relation

$$F[c_1 f_1 + c_2 f_2] = c_1 F[f_1] + c_2 F[f_2]\,, \tag{A.7}$$

with c_1, c_2 being complex numbers. Examples of nonlinear functionals are:

- The energy functional of the simplest DFT, the Thomas-Fermi kinetic energy,

$$F_{\mathrm{TF}}[n] \equiv T_{\mathrm{s}}^{\mathrm{TF}}[n] = C_{\mathrm{TF}} \int d^3 r\, n^{5/3}(\boldsymbol{r})\,. \tag{A.8}$$

- A nonlocal functional of two functions,

$$F_w[f_1, f_2] = \int f_1(x_1) w(x_1, x_2) f_2(x_2) dx_1 dx_2\,. \tag{A.9}$$

- The action integral of classical mechanics,

$$F[\boldsymbol{q}] \equiv A[\boldsymbol{q}] = \int_{t_1}^{t_2} dt\, L(\boldsymbol{q}(t), \dot{\boldsymbol{q}}(t), t)\,. \tag{A.10}$$

The abbreviation $\boldsymbol{q}(t)$ stands for a set of generalized coordinates, which depend on time.

- Any matrix element of quantum mechanics, e.g. the ground state energy and the S-matrix element of potential scattering theory,

$$F[\Psi_0, \Psi_0^*] \equiv E[\Psi_0, \Psi_0^*] = \int d^3 r\, \Psi_0^*(\boldsymbol{r}) \hat{H} \Psi_0(\boldsymbol{r})$$

$$F[\Psi_{\boldsymbol{k}}, \Psi_{\boldsymbol{q}}^*] \equiv S[\Psi_{\boldsymbol{k}}, \Psi_{\boldsymbol{q}}^*] = \int d^3 r\, \Psi_{\boldsymbol{q}}^*(\boldsymbol{r}) \hat{S} \Psi_{\boldsymbol{k}}(\boldsymbol{r})\,.$$

It seems worthwhile to emphasize that the two functions Ψ_0 and Ψ_0^* have to be considered as being independent, so that one is dealing with a functional of two functions. Alternatively, a dependence on the real and the imaginary part of the wavefunctions can be used to characterize the functional.

A.2 Functional Derivative

Usually knowledge of the complete functional $F[f]$, as for example the classical action $A[\boldsymbol{q}]$ for all possible trajectories in phase space or the value of the integral (A.3) for all continuous functions, is not required. Rather it is the behavior of the functional in the vicinity of the function f_0, which makes $F[f]$ extremal or stationary, which is of interest.[1] The implementation of the search for f_0 involves the exploration of the space of functions in the vicinity of f_0 in a suitable fashion.

A variation of any function f by an infinitesimal but arbitrary amount can be represented in the form

$$\begin{aligned} \delta f(x) &= \varepsilon\,\eta(x) && \text{for one variable} \\ \delta f(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots) &= \varepsilon\,\eta(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots) && \text{for several variables .} \end{aligned} \tag{A.11}$$

The quantity ε is an infinitesimal number, η is an arbitrary function. In order to explore the properties of the functionals a generalization of the (ordinary or partial) derivative (of first and higher order)—the functional derivative—is required. It can be defined via the variation δF of the functional $F[f]$ which results from variation of f by δf,

$$\delta F := F[f+\delta f] - F[f]\,. \tag{A.12}$$

The technique used to evaluate δF is a Taylor expansion of the functional $F[f+\delta f] = F[f+\varepsilon\eta]$ in powers of δf, respectively of ε. The functional $F[f+\varepsilon\eta]$ is an ordinary function of ε. This implies that the expansion in terms of powers of ε is a standard Taylor expansion,

$$F[f+\varepsilon\,\eta] = F[f] + \left.\frac{dF[f+\varepsilon\eta]}{d\varepsilon}\right|_{\varepsilon=0}\varepsilon + \frac{1}{2}\left.\frac{d^2F[f+\varepsilon\eta]}{d\varepsilon^2}\right|_{\varepsilon=0}\varepsilon^2 + \ldots \tag{A.13}$$

$$= \sum_{n=0}^{N}\frac{1}{n!}\left.\frac{d^nF[f+\varepsilon\eta]}{d\varepsilon^n}\right|_{\varepsilon=0}\varepsilon^n + \mathscr{O}\left(\varepsilon^{N+1}\right)\,. \tag{A.14}$$

As indicated, the sum in (A.14) can be finite or infinite. In the latter case, it has to be assumed that the function $F(\varepsilon)$ can be differentiated with respect to ε any number of times.

[1] Often functionals are introduced to recast some equation(s) in the form of an extremum or stationarity principle.

The derivatives with respect to ε now have to be related to the functional derivatives. This is achieved by a suitable definition. The definition of the functional derivative (also called variational derivative) is

$$\left.\frac{dF[f+\varepsilon\eta]}{d\varepsilon}\right|_{\varepsilon=0} =: \int dx_1 \, \frac{\delta F[f]}{\delta f(x_1)} \, \eta(x_1) \, . \tag{A.15}$$

This definition implies that the left-hand side can be brought into the form on the right-hand side, i.e. the form of a linear functional with kernel $\delta F[f]/\delta f$ acting on the test function η. This is by no means guaranteed for arbitrary functionals and arbitrary f. It is exactly this point where rigorous mathematics sets in. A functional for which (A.15) is valid is called *differentiable*.[2] We will, however, not go into any details concerning the existence of the functional derivative, nor will we make any attempt to characterize the space of (test) functions which are allowed in (A.15) (as usual, the existence of all integrals involved is assumed, of course).

The definition (A.15) can be thought of as an extension of the first total differential of a function of several variables,

$$f(x_1, x_2, \ldots) \quad \longrightarrow \quad df = \sum_{n=1}^{N} \frac{\partial f}{\partial x_n} \, dx_n \, ,$$

to the case of an infinite set of variables $f(x_1)$. The definition of the second order functional derivative corresponds to the second order total differential,

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[2] More precisely, a functional $F[f]$ which maps an open subset of some Banach space $\mathscr{X}$ (i.e. some complete normed vector space) of functions f onto another Banach space $\mathscr{Y}$ (which could be the set of real or complex numbers) is called *Fréchet differentiable*, if there exists a linear continuous operator $\delta F_f^{\mathrm{F}} : \mathscr{X} \to \mathscr{Y}$ with the property

$$\lim_{\|\eta\|\to 0} \frac{\|F[f+\eta] - F[f] - \delta F_f^{\mathrm{F}}[\eta]\|_{\mathscr{Y}}}{\|\eta\|_{\mathscr{X}}} = 0 \, .$$

Here $\|F\|_{\mathscr{Y}}$ and $\|\eta\|_{\mathscr{X}}$ denote the norms in the two Banach spaces. The Fréchet derivative has to be distinguished from the Gâteaux derivative, which exists if there is a linear continuous operator $\delta F_f^{\mathrm{G}} : \mathscr{X} \to \mathscr{Y}$ such that

$$\delta F_f^{\mathrm{G}}[\eta] = \lim_{\lambda\to 0} \frac{\|F[f+\lambda\eta] - F[f]\|_{\mathscr{Y}}}{\lambda} \, .$$

If the right-hand side of this relation exists, but does not yield a linear continuous operator, it is called the Gâteaux differential,

$$F'[f,\eta] = \lim_{\lambda\to 0} \frac{\|F[f+\lambda\eta] - F[f]\|_{\mathscr{Y}}}{\lambda} .$$

Thus any Fréchet differentiable functional is also Gâteaux differentiable, but the converse is not true. The existence of the Fréchet derivative is only ensured, if the Gâteaux derivative is continuous or if the Gâteaux differential is uniform with respect to η with $\|\eta\| = 1$.

$$\left.\frac{d^2F[f+\varepsilon\eta]}{d\varepsilon^2}\right|_{\varepsilon=0} =: \int dx_1 dx_2 \, \frac{\delta^2 F[f]}{\delta f(x_1)\delta f(x_2)} \, \eta(x_1)\eta(x_2) \, . \tag{A.16}$$

The definition of the general derivative can be guessed at this stage. The functional derivative of n-th order is given by

$$\left.\frac{d^nF[f+\varepsilon\eta]}{d\varepsilon^n}\right|_{\varepsilon=0} =: \int dx_1 \ldots dx_n \, \frac{\delta^n F[f]}{\delta f(x_1)\ldots\delta f(x_n)} \, \eta(x_1)\ldots\eta(x_n) \, . \tag{A.17}$$

This derivative constitutes the kernel of the Taylor expansion of a functional F in terms of the variation $\delta f(x) = \varepsilon\eta(x)$,

$$\begin{aligned} F[f+\varepsilon\eta] = \sum_{n=0}^{N} \frac{1}{n!} \int dx_1 \ldots dx_n \, \frac{\delta^n F[f]}{\delta f(x_1)\ldots\delta f(x_n)} \, \delta f(x_1)\ldots\delta f(x_n) \\ + \mathscr{O}\left(\varepsilon^{N+1}\right) \, , \end{aligned} \tag{A.18}$$

again with N being either finite or infinite.

The actual calculation of the functional derivative relies on the evaluation of the difference (A.12). This will be illustrated with the aid of a few examples.

- According to Eq. (A.12), the variation of the functional (A.6) is

  $$\delta F_\delta = \int_{x_1}^{x_2} \delta(x-x_0)\varepsilon\eta(x)dx \, .$$

  Comparison with the definition (A.15) shows that

  $$\frac{\delta F_\delta}{\delta f(x)} = \delta(x-x_0) \, , \tag{A.19}$$

  as $\eta(x)$ can vary freely. A very useful formula is obtained if the definition

  $$F_\delta[f] = f(x_0)$$

  is used explicitly,

  $$\frac{\delta F_\delta}{\delta f(x)} = \frac{\delta f(x_0)}{\delta f(x)} = \delta(x-x_0) \, . \tag{A.20}$$

  All higher order functional derivatives of F_δ vanish.
- This example is readily extended to the functional

  $$f(x_0)^\alpha = \int dx \, \delta(x-x_0) \, f(x)^\alpha \, .$$

  Its variation can be evaluated by straightforward Taylor expansion,

  $$\delta f(x_0)^\alpha = \int dx \, \delta(x-x_0) \, [(f(x)+\varepsilon\eta(x))^\alpha - f(x)^\alpha]$$

$$= \int dx\, \delta(x-x_0) \Big[\alpha f(x)^{\alpha-1} \varepsilon\eta(x) + \frac{\alpha(\alpha-1)}{2} f(x)^{\alpha-2} (\varepsilon\eta(x))^2 + \ldots \Big] .$$

The functional derivative is again identified by comparison with the definition (A.15),

$$\frac{\delta f(x_0)^\alpha}{\delta f(x)} = \delta(x-x_0)\, \alpha f(x)^{\alpha-1} . \tag{A.21}$$

In order to calculate the second functional derivative one can simply reuse Eq. (A.21),

$$\frac{\delta^2 f(x_0)^\alpha}{\delta f(x_1) \delta f(x_2)} = \delta(x_1-x_0)\, \delta(x_2-x_0)\, \alpha(\alpha-1) f(x)^{\alpha-2} . \tag{A.22}$$

- The variation of the Thomas-Fermi functional (A.8) is obtained from

$$\delta F_{\mathrm{TF}} = C_{\mathrm{TF}} \int d^3 r \left[(n(\boldsymbol{r}) + \varepsilon\eta(\boldsymbol{r}))^{5/3} - n(\boldsymbol{r})^{5/3} \right]$$

in the form of a binomial expansion

$$\delta F_{\mathrm{TF}} = C_{\mathrm{TF}} \int d^3 r\, n(\boldsymbol{r})^{5/3} \sum_{k=1}^{\infty} \binom{5/3}{k} \left(\frac{\varepsilon\eta(\boldsymbol{r})}{n(\boldsymbol{r})} \right)^k .$$

The functional derivatives, which can be extracted from this expression, are

$$\frac{\delta F_{\mathrm{TF}}}{\delta n(\boldsymbol{r})} = \frac{5}{3} C_{\mathrm{TF}}\, n(\boldsymbol{r})^{2/3} \tag{A.23}$$

for the first derivative and, applying (A.21),

$$\frac{\delta^2 F_{\mathrm{TF}}}{\delta n(\boldsymbol{r}) \delta n(\boldsymbol{r}')} = \frac{10}{9} C_{\mathrm{TF}}\, n(\boldsymbol{r})^{-1/3}\, \delta^{(3)}(\boldsymbol{r}-\boldsymbol{r}')$$

for the second derivative.

- The variation of the nonlocal functional

$$F_w[f] = \int_{y_1}^{y_2} dx_1 \int_{y_1}^{y_2} dx_2\, f(x_1) w(x_1,x_2) f(x_2) \tag{A.24}$$

is

$$\delta F_w = \int_{y_1}^{y_2} dx_1 \int_{y_1}^{y_2} dx_2\, w(x_1,x_2) [f(x_1)\varepsilon\eta(x_2) + f(x_2)\varepsilon\eta(x_1) + \varepsilon\eta(x_1)\varepsilon\eta(x_2)] . \tag{A.25}$$

The variational derivatives are

$$\frac{\delta F_w}{\delta f(x)} = \int_{y_1}^{y_2} dx_2 \, [w(x,x_2) + w(x_2,x)] f(x_2) \tag{A.26}$$

and

$$\frac{\delta^2 F_w}{\delta f(x_1) f(x_2)} = w(x_1,x_2) + w(x_2,x_1) \, . \tag{A.27}$$

All derivatives with $n > 2$ vanish for this example.

A.3 Calculational Rules

The calculation of the functional derivative can be abbreviated using a variation in terms of the δ-function: for the functionals relevant in physics all local, δ-type variations of $f(x)$ are equivalent to probing the functional with arbitrary general variations $\eta(x)$. The functional derivative can therefore be recast in the form of the (almost familiar) limiting value

$$\frac{\delta F}{\delta f(x_1)} = \lim_{\varepsilon \to 0} \frac{F[f(x) + \varepsilon \delta(x - x_1)] - F[f(x)]}{\varepsilon} \, . \tag{A.28}$$

The reader may check that this form follows from the definition (A.15) with the replacement $\eta(x) \longrightarrow \delta(x - x_1)$ and that it reproduces the results of the examples. When using the form (A.28), one has to remember that the variation $\delta f = \varepsilon \delta(x - x_1)$ should always be understood in the sense of a representation of the δ-function via some sequence of regular functions, so that powers of the δ-function are uncritical.

As the functional derivatives constitute an extension of the concept of the ordinary derivative, most of the rules for ordinary derivatives can be taken over. For example, the product rule of functional differentiation can be obtained directly with the argument

$$\begin{aligned} \left[\frac{d(F_1[f + \varepsilon\eta] F_2[f + \varepsilon\eta])}{d\varepsilon} \right]_{\varepsilon=0} &= \left[\frac{dF_1[f + \varepsilon\eta]}{d\varepsilon} F_2[f + \varepsilon\eta] \right]_{\varepsilon=0} \\ &\quad + \left[F_1[f + \varepsilon\eta] \frac{dF_2[f + \varepsilon\eta]}{d\varepsilon} \right]_{\varepsilon=0} , \end{aligned}$$

which is valid as F_1 and F_2 are *functions* of ε. In the actual limit $\varepsilon \to 0$ there follows with (A.15)

$$\frac{\delta(F_1 F_2)}{\delta f(x)} = \frac{\delta F_1}{\delta f(x)} F_2 + F_1 \frac{\delta F_2}{\delta f(x)} \, . \tag{A.29}$$

Let us next extend the chain rule for functions to functionals. Consider a functional F which depends on some function $G(y)$, which itself is a functional of $f(x)$, $G[f](y)$. The functional F therefore is also a functional of $f(x)$. Its variation with f is then given by

$$\begin{aligned}\delta F_f &= F[G[f(x)+\varepsilon\eta(x)](y)] - F[G[f(x)](y)] \\ &= \left.\frac{dF[G[f(x)+\varepsilon\eta(x)](y)]}{d\varepsilon}\right|_{\varepsilon=0} \varepsilon + \mathcal{O}(\varepsilon^2) \qquad \text{(A.30)} \\ &= \int \frac{\delta F[f]}{\delta f(x)}\,\varepsilon\eta(x)\,dx + \mathcal{O}(\varepsilon^2)\,, \qquad \text{(A.31)}\end{aligned}$$

where the last line simply represents the definition of the functional derivative of F with respect to f, according to Eq. (A.15). Similarly, the variation of G with f is obtained as

$$\begin{aligned}\delta G(y) &= G[f(x)+\varepsilon\eta(x)](y) - G[f(x)](y) \\ &= \left.\frac{dG[f(x)+\varepsilon\eta(x)](y)}{d\varepsilon}\right|_{\varepsilon=0} \varepsilon + \mathcal{O}(\varepsilon^2) \qquad \text{(A.32)} \\ &= \int \frac{\delta G[f](y)}{\delta f(x)}\,\varepsilon\eta(x)\,dx + \mathcal{O}(\varepsilon^2)\,. \qquad \text{(A.33)}\end{aligned}$$

Now, to first order in ε one can express $G[f(x)+\varepsilon\eta(x)](y)$ via Eq. (A.33),

$$G[f(x)+\varepsilon\eta(x)](y) = G[f(x)](y) + \int \frac{\delta G[f](y)}{\delta f(x)}\,\varepsilon\eta(x)\,dx + \mathcal{O}(\varepsilon^2)\,,$$

to obtain

$$\begin{aligned}\int \frac{\delta F[f]}{\delta f(x)}\,\eta(x)\,dx = &\left.\frac{dF[G[f(x)](y) + \int \frac{\delta G[f](y)}{\delta f(x)}\varepsilon\eta(x)dx + \mathcal{O}(\varepsilon^2)]}{d\varepsilon}\right|_{\varepsilon=0} \\ &+\mathcal{O}(\varepsilon)\,. \qquad \text{(A.34)}\end{aligned}$$

However, the derivative on the right-hand side has exactly the form of the variation of F with G,

$$\begin{aligned}\delta F_G &= F[G(y)+\varepsilon\bar{\eta}(y)] - F[G(y)] \\ &= \left.\frac{dF[G(y)+\varepsilon\bar{\eta}(y)]}{d\varepsilon}\right|_{\varepsilon=0} \varepsilon + \mathcal{O}(\varepsilon^2)\,, \qquad \text{(A.35)}\end{aligned}$$

with $\bar{\eta}$ given by

$$\bar{\eta}(y) = \int \frac{\delta G[f](y)}{\delta f(x)}\,\eta(x)dx\,. \qquad \text{(A.36)}$$

Provided that $\bar{\eta}(y)$ probes the complete space around $G(y)$, in which $F[G]$ is defined, when $\eta(x)$ goes through all legitimate variations of $f(x)$, the expression (A.34) coincides with the corresponding functional derivative of F with respect to $G(y)$,

$$\left.\frac{dF[G(y)+\varepsilon\bar{\eta}(y)]}{d\varepsilon}\right|_{\varepsilon=0} = \int \frac{\delta F[G]}{\delta G(y)}\,\bar{\eta}(y)\,dy + \mathscr{O}(\varepsilon)\,. \tag{A.37}$$

Combination of Eqs. (A.34), (A.36) and (A.37) finally yields

$$\int \frac{\delta F[f]}{\delta f(x)}\,\eta(x)\,dx = \int \frac{\delta F[G]}{\delta G(y)}\,\frac{\delta G[f](y)}{\delta f(x)}\,\eta(x)\,dxdy\,,$$

and thus, due to the arbitrary form of $\eta(x)$,

$$\frac{\delta F[f]}{\delta f(x)} = \int \frac{\delta F[G]}{\delta G(y)}\,\frac{\delta G[f](y)}{\delta f(x)}\,dy\,. \tag{A.38}$$

Equation (A.38) represents the chain rule of functional differentiation. It is valid, if the variation $\eta(x)$ generates all possible variations $\bar{\eta}(y)$ in the neighborhood of $G[f](y)$. This is guaranteed if there is a one-to-one correspondence between the admissible functions $f(x)$ and the corresponding functions $G(y)$ (at least locally) and both spaces of functions are sufficiently dense to define a functional derivative. The condition of a unique correspondence is satisfied in particular, if the kernel $\frac{\delta G[f](y)}{\delta f(x)}$ is invertible.

It is worthwhile to note a special case of the rule (A.38). If there is a unique relation between $f(x)$ and $G(y)$, i.e. if the form of the complete function $G(y)$ is uniquely determined by $f(x)$ and vice versa, one can consider the functional $F[G[f(x)](y)] \equiv f(x_0)$. Application of the chain rule (A.38) then leads to

$$\begin{aligned}\delta(x-x_0) = \frac{\delta f(x_0)}{\delta f(x)} &= \frac{\delta F[f]}{\delta f(x)} = \int \frac{\delta F[G]}{\delta G(y)}\,\frac{\delta G[f](y)}{\delta f(x)}\,dy \\ &= \int \frac{\delta f(x_0)}{\delta G(y)}\,\frac{\delta G(y)}{\delta f(x)}\,dy\,.\end{aligned} \tag{A.39}$$

This relation shows that one can always insert a complete set of variations in a variational derivative (here $\delta f(x_0)/\delta f(x)$), as long as there exists a one-to-one correspondence between the functions involved.

A.4 Variational Principle

An apt example for the discussion of variational principles on the basis of functional calculus is the derivation of the Euler-Lagrange equations for the action functional (A.10). For the case of one degree of freedom,

$$A[q] = \int_{t_1}^{t_2} dt\, L(q, \dot{q}, t)\ , \tag{A.40}$$

which suffices to point out the main features, extrema are characterized by setting the first variation equal to zero. This implies

$$\delta A = \int_{t_1}^{t_2} dt\, [L(q + \delta q, \dot{q} + \delta \dot{q}, t) - L(q, \dot{q}, t)] = 0 \tag{A.41}$$

to first order in the variation of the variable and its derivative. Taylor expansion of the first term to first order gives

$$\delta A = \int_{t_1}^{t_2} dt\, \left[\frac{\partial L}{\partial q} \delta q + \frac{\partial L}{\partial \dot{q}} \delta \dot{q} \right] = 0\ . \tag{A.42}$$

This is followed by partial integration of the second term with the result

$$\delta A = \int_{t_1}^{t_2} dt\, \left[\frac{\partial L}{\partial q} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}} \right] \delta q + \left[\frac{\partial L}{\partial \dot{q}} \delta q \right]_{t_1}^{t_2} = 0\ . \tag{A.43}$$

For arbitrary variations δq the Euler-Lagrange equations have to be satisfied,

$$\frac{\partial L}{\partial q} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}} = 0\ . \tag{A.44}$$

No further conditions apply, if the variation at the end points is restricted by boundary conditions,

$$\delta q(t_1) = \delta q(t_2) = 0\ . \tag{A.45}$$

This restriction does not apply to the case of a free boundary, for which arbitrary variations at the points t_1 and t_2 are permitted. Therefore it is necessary to demand in addition the "natural boundary conditions" (see [728])

$$\left[\frac{\partial L}{\partial \dot{q}} \right]_{t_1} = \left[\frac{\partial L}{\partial \dot{q}} \right]_{t_2} = 0 \tag{A.46}$$

in this case.

Appendix B
Second Quantization in Many-Body Theory

The language of second quantization allows a compact formulation of quantum many-particle problems. The name "second quantization" arose actually in the context of quantum field theory, where the need to accommodate particle creation or annihilation processes demanded the replacement of wavefunctions by operators. This Appendix provides an introduction to this tool tailored to the requirements of many-body theory.

B.1 *N*-Particle Hilbert Space

B.1.1 Realization in First Quantized Form

The basic elements of the discussion are square-integrable single-particle wavefunctions in configuration or configuration-spin space. These functions span the 1-particle Hilbert space $\mathscr{H}_1$. They will be denoted by

$$\phi_\alpha(x)\ . \tag{B.1}$$

The index α represents a set of quantum numbers, which characterize the state of the particle completely, as e.g. the quantum numbers of the nonrelativistic hydrogen problem,

$$\alpha \longrightarrow n, l, m, m_s\ . \tag{B.2}$$

For the present purpose it is most convenient to characterize the states by a single discrete label which orders all states in a well-defined sequence.

The variable x in Eq. (B.1) stands for the spatial coordinates $\boldsymbol{r}$ and, if applicable, additional internal degrees of freedom. A relevant example are the components of the bispinor wavefunction of a spin-$1/2$ fermion,

$$\phi_\alpha(x) = \phi_\alpha(\boldsymbol{r}\sigma) = \begin{cases} \phi_\alpha(\boldsymbol{r}, +\frac{1}{2}) & \text{if } \sigma = +\frac{1}{2} \equiv \uparrow \\ \phi_\alpha(\boldsymbol{r}, -\frac{1}{2}) & \text{if } \sigma = -\frac{1}{2} \equiv \downarrow \end{cases} . \tag{B.3}$$

For brevity the complex functions (B.1) are supposed to be orthonormal

$$\int dx\, \phi^*_\alpha(x)\phi_\beta(x) = \delta_{\alpha\beta} . \tag{B.4}$$

The integral $\int dx$ abbreviates integration over space and summation over all internal degrees of freedom, as e.g. in the case of spin-1/2 fermions

$$\int dx \equiv \sum_{\sigma=\uparrow,\downarrow} \int d^3r .$$

In addition, the functions $\phi_\alpha(x)$ are assumed to form a complete set,

$$\sum_\alpha \phi_\alpha(x)\phi^*_\alpha(x') = \delta^{(3)}(\boldsymbol{r}-\boldsymbol{r}')\,\delta_{\sigma,\sigma'} \equiv \delta(x,x') . \tag{B.5}$$

The Hilbert space $\mathscr{H}_N$ of N identical particles is the *tensor product* of N single-particle Hilbert spaces,

$$\mathscr{H}_N = \mathscr{H}_1 \otimes \mathscr{H}_1 \otimes \cdots \otimes \mathscr{H}_1 . \tag{B.6}$$

This space is spanned by the product wavefunctions

$$\Phi^{\mathrm{c}}_{\alpha_1\cdots\alpha_N}(x_1 x_2 \cdots x_N) = \phi_{\alpha_1}(x_1)\phi_{\alpha_2}(x_2)\cdots\phi_{\alpha_N}(x_N) . \tag{B.7}$$

In these *canonical* N-particle states particle number 1 with coordinates $\boldsymbol{r}_1$ and spin-projection σ_1 is in the single-particle state α_1, particle number 2 at x_2 in state α_2, and so on. Orthonormality and completeness of this basis of $\mathscr{H}_N$ follow from the corresponding properties of the 1-particle functions,

$$\begin{aligned} &\int dx_1\cdots dx_N\, \Phi^{\mathrm{c}\,*}_{\alpha_1\cdots\alpha_N}(x_1\cdots x_N)\Phi^{\mathrm{c}}_{\beta_1\cdots\beta_N}(x_1\cdots x_N) \\ &= \int dx_1\, \phi^*_{\alpha_1}(x_1)\phi_{\beta_1}(x_1)\cdots\int dx_N\, \phi^*_{\alpha_N}(x_N)\phi_{\beta_N}(x_N) \\ &= \delta_{\alpha_1\beta_1}\cdots\delta_{\alpha_N\beta_N} \end{aligned} \tag{B.8}$$

$$\begin{aligned} &\sum_{\alpha_1\cdots\alpha_N} \Phi^{\mathrm{c}}_{\alpha_1\cdots\alpha_N}(x_1\cdots x_N)\Phi^{\mathrm{c}\,*}_{\alpha_1\cdots\alpha_N}(y_1\cdots y_N) \\ &= \sum_{\alpha_1}\phi_{\alpha_1}(x_1)\phi^*_{\alpha_1}(y_1)\cdots\sum_{\alpha_N}\phi_{\alpha_N}(x_N)\phi^*_{\alpha_N}(y_N) \\ &= \delta(x_1,y_1)\cdots\delta(x_N,y_N) . \end{aligned} \tag{B.9}$$

The states $\Phi^{\mathrm{c}}_{\alpha_1\cdots\alpha_N}$ are ordered with respect to the particles and their labels, which is only possible if the individual particles can be distinguished. However, in the

case of N identical quantum particles, their fermionic or bosonic nature has to be taken into account, so that only the corresponding subspaces $\mathscr{F}_N$ and $\mathscr{B}_N$ of $\mathscr{H}_N$ are of interest. The wavefunctions of the fermion sector, to which we restrict the discussion, are antisymmetric: *any* wavefunction Ψ describing N identical fermions satisfies the relation

$$\Psi(x_{p_1}\cdots x_{p_N}) = (-1)^P \Psi(x_1\cdots x_N)\,, \tag{B.10}$$

where $p_1,\ldots p_N$ denotes an arbitrary permutation of the numbers $1,\ldots N$. The sign of the permutations $(-1)^P$ corresponds to the property even $(+)$ or odd $(-)$, according to the number P of pairwise transpositions necessary to restore the natural order.[1]

A basis in $\mathscr{F}_N$ can be constructed from the canonical basis by explicit antisymmetrization,

$$\begin{aligned}\Phi_{\alpha_1\cdots\alpha_N}(x_1x_2\cdots x_N) &= \frac{1}{\sqrt{N!}}\sum_{P\in S_N}(-1)^P \Phi^{\mathrm{c}}_{\alpha_{p_1}\cdots\alpha_{p_N}}(x_1x_2\cdots x_N)\\ &= \frac{1}{\sqrt{N!}}\sum_{P\in S_N}(-1)^P \phi_{\alpha_{p_1}}(x_1)\phi_{\alpha_{p_2}}(x_2)\cdots\phi_{\alpha_{p_N}}(x_N)\\ &= \frac{1}{\sqrt{N!}}\sum_{P\in S_N}(-1)^P \phi_{\alpha_1}(x_{p_1})\phi_{\alpha_2}(x_{p_2})\cdots\phi_{\alpha_N}(x_{p_N})\,. \end{aligned}\tag{B.11}$$

The sum runs over all permutations of N ordered objects. This set of permutations constitutes the symmetric group S_N. The last lines indicate that the basis functions of $\mathscr{F}_N$ take the form of a determinant—a *Slater determinant*.

The antisymmetrized states $\Phi_{\alpha_1\cdots\alpha_N}$ do no longer associate a particular single-particle quantum number with a given particle. Their determinantal structure is a direct manifestation of the Pauli principle which is expressed by Eq. (B.10). The function $\Phi_{\alpha_1\cdots\alpha_N}$ vanishes if two of the labels $\alpha_1\cdots\alpha_N$ are identical. This allows a definite (although arbitrary) ordering of the quantum numbers in $\Phi_{\alpha_1\cdots\alpha_N}$ in the form $\alpha_1<\alpha_2\cdots<\alpha_N$.

The basis functions (B.11) are orthonormal and complete in $\mathscr{F}_N$, provided the 1-particle basis is orthonormal and complete in $\mathscr{H}_1$. For the illustration of orthonormality one simply uses the definition (B.11),

$$\begin{aligned}&\int dx_1\cdots dx_N\,\Phi^*_{\alpha_1\cdots\alpha_N}(x_1\cdots x_N)\Phi_{\beta_1\cdots\beta_N}(x_1\cdots x_N)\\ &= \frac{1}{N!}\sum_{P,P'\in S_N}(-1)^{P+P'}\int dx_1\,\phi^*_{\alpha_{p_1}}(x_1)\phi_{\beta_{p'_1}}(x_1)\cdots\int dx_N\,\phi^*_{\alpha_{p_N}}(x_N)\phi_{\beta_{p'_N}}(x_N)\\ &= \frac{1}{N!}\sum_{P,P'\in S_N}(-1)^{P+P'}\delta_{\alpha_{p_1}\beta_{p'_1}}\cdots\delta_{\alpha_{p_N}\beta_{p'_N}}\,.\end{aligned}$$

[1] A given permutation can be generated by different sequences of pairwise transpositions. However, the number of pairwise transpositions required is uniquely either even or odd.

The sum over the permutations P' in the last line yields, for a given permutation P, exactly the same terms that are obtained with the regular ordering $1,2,\ldots N$. The sign that is required to bring a given permutation $p'_1,\ldots p'_N$ into the natural order is just $(-1)^{P'}$. One can therefore eliminate the multiplicity by arranging the first indices of the Kronecker symbols in regular order and sum only over all the permutations of the second,

$$\begin{aligned}
&\int dx_1 \cdots dx_N \, \Phi^*_{\alpha_1\cdots\alpha_N}(x_1\cdots x_N)\,\Phi_{\beta_1\cdots\beta_N}(x_1\cdots x_N) \\
&= \sum_{P\in S_N} (-1)^P \delta_{\alpha_1\beta_{p_1}}\cdots\delta_{\alpha_N\beta_{pN}} \\
&= \det\begin{pmatrix} \langle\alpha_1|\beta_1\rangle & \cdots & \langle\alpha_1|\beta_N\rangle \\ \vdots & \vdots & \vdots \\ \langle\alpha_N|\beta_1\rangle & \cdots & \langle\alpha_N|\beta_N\rangle \end{pmatrix} . \qquad \text{(B.12)}
\end{aligned}$$

The final result takes the form of a determinant. It becomes simpler, if the state labels are arranged in a given order. For

$$\alpha_1 < \alpha_2 < \cdots < \alpha_N \qquad \text{and} \qquad \beta_1 < \beta_2 < \cdots < \beta_N \qquad \text{(B.13)}$$

one obtains

$$\int dx_1 \cdots dx_N \, \Phi^*_{\alpha_1\cdots\alpha_N}(x_1\cdots x_N)\,\Phi_{\beta_1\cdots\beta_N}(x_1\cdots x_N) \;=\; \delta_{\alpha_1\beta_1}\cdots\delta_{\alpha_N\beta_N} . \qquad \text{(B.14)}$$

The completeness relation follows in a similar fashion

$$\begin{aligned}
&\sum_{\alpha_1\cdots\alpha_N} \Phi_{\alpha_1\cdots\alpha_N}(x_1\cdots x_N)\Phi^*_{\alpha_1\cdots\alpha_N}(y_1\cdots y_N) \\
&= \frac{1}{N!}\sum_{P,P'\in S_N} (-1)^{P+P'} \left\{\sum_{\alpha_1}\phi_{\alpha_1}(x_{p_1})\phi^*_{\alpha_1}(y_{p'_1})\right\}\cdots\left\{\sum_{\alpha_N}\phi_{\alpha_N}(x_N)\phi^*_{\alpha_N}(y_{p'_N})\right\} \\
&= \frac{1}{N!}\sum_{P,P'\in S_N} (-1)^P(-1)^{P'}\delta(x_{p_1},y_{p'_1})\cdots\delta(x_{p_N},y_{p'_N}) \\
&= \sum_{P\in S_N} (-1)^P \delta(x_1,y_{p_1})\cdots\delta(x_N,y_{p_N}) . \qquad \text{(B.15)}
\end{aligned}$$

The transition from the second to last to the last line involves the same argument concerning the multiplicity of terms as in the case of the orthogonality relation.

The derivation of the completeness relation has to be augmented by one additional point: one has to take into account the fact that the operator

$$\sum_{\alpha_1\cdots\alpha_N} \Phi_{\alpha_1\cdots\alpha_N}(x_1\cdots)\Phi^*_{\alpha_1\cdots\alpha_N}(y_1\cdots)$$

acts only on the antisymmetric states in $\mathscr{F}_N$. If a product of Kronecker symbols, as in (B.15), is contracted with an arbitrary antisymmetric wavefunction Ψ, the permutation of the coordinates $y_1, \ldots y_N$ leads to

$$\int dy_1 \cdots dy_N \, \delta(x_1, y_{p_1}) \cdots \delta(x_N, y_{p_N}) \Psi(y_1 \cdots y_N) \;=\; (-1)^P \Psi(x_1 \cdots x_N) \,. \quad \text{(B.16)}$$

Within the space $\mathscr{F}_N$ one thus obtains

$$\sum_{\alpha_1 \cdots \alpha_N} \Phi_{\alpha_1 \cdots \alpha_N}(x_1 \cdots x_N) \, \Phi^*_{\alpha_1 \cdots \alpha_N}(y_1 \cdots y_N) \;=\; N! \, \delta(x_1, y_1) \cdots \delta(x_N, y_N) \,. \quad \text{(B.17)}$$

The factor $N!$ results from the overcompleteness of the basis set formed by the $\Phi_{\alpha_1 \cdots \alpha_N}$ in the space $\mathscr{F}_N$: since all states $\Phi_{\alpha_1 \cdots \alpha_N}$ which differ only by a permutation of the set $\alpha_1, \ldots \alpha_N$ coincide (up to an irrelevant sign), any basis state shows up $N!$ times in the sum on the left-hand side of Eq. (B.17). The factor is easily eliminated by use of an ordered sum,

$$\sum_{\alpha_1 < \alpha_2 \cdots < \alpha_N} \Phi_{\alpha_1 \cdots \alpha_N}(x_1 \cdots x_N) \, \Phi^*_{\alpha_1 \cdots \alpha_N}(y_1 \cdots y_N) \;=\; \delta(x_1, y_1) \cdots \delta(x_N, y_N) \,. \quad \text{(B.18)}$$

B.1.2 Formal Representation

The same statements can be made on a more formal level, if one adopts the *Dirac notation*.

The discussion of the formal representation also begins with a look at the Hilbert space of one particle, $\mathscr{H}_1$. The 1-particle wavefunctions are interpreted as a scalar product of two state vectors $|x\rangle$ and $|\alpha\rangle \equiv |\phi_\alpha\rangle$ which is written as

$$\phi_\alpha(x) \equiv \langle x | \alpha \rangle \,. \quad \text{(B.19)}$$

A state vector of the form $\langle x|$ is called a *bra-vector*, of the form $|\alpha\rangle$ a *ket-vector*. The scalar product itself is therefore often referred to as a *bra-ket*. Since Eq. (B.19) relates the wavefunction to a scalar product, one finds for the complex conjugate wavefunction,

$$\phi^*_\alpha(x) = \langle \alpha | x \rangle \,. \quad \text{(B.20)}$$

The state $\langle \alpha|$ is the adjoint of the state $|\alpha\rangle$.

The set of vectors $|\alpha\rangle$ and the set $|x\rangle$ are elements of different vector spaces. The notation implies that "factors" with the label α carry the information concerning the quantum labels, "factors" with x define the representation space of the particle as position and spin space. The separation of the wavefunction in terms of two abstract ingredients allows, for example, an easy transition to alternative representation spaces as the momentum-spin space.

The states $|\alpha\rangle$ span the familiar Hilbert space $\mathscr{H}_1$. They form a complete and orthonormal set. This is expressed by the relations[2]

$$\sum_\alpha |\alpha\rangle\langle\alpha| = \hat{1}_{\mathscr{H}_1} ; \qquad \langle\alpha|\beta\rangle = \delta_{\alpha\beta} . \tag{B.21}$$

The consistency of these relations can be checked by considering

$$\langle x|\alpha\rangle = \sum_\beta \langle x|\beta\rangle\langle\beta|\alpha\rangle = \sum_\beta \langle x|\beta\rangle\delta_{\alpha\beta} = \langle x|\alpha\rangle .$$

The vector $|x\rangle \equiv |\boldsymbol{r}\sigma\rangle$ is an eigenstate of the position operator $\hat{\boldsymbol{r}}$ and the spin-projection operator $\hat{s}_z$. It is characterized by the corresponding eigenvalues $\boldsymbol{r}$ and $\sigma = \pm 1$,

$$\hat{\boldsymbol{r}}|x\rangle = \boldsymbol{r}\,|x\rangle \tag{B.22}$$

$$\hat{s}_z|x\rangle = \sigma\frac{\hbar}{2}\,|x\rangle . \tag{B.23}$$

The notation indicates that operators $\hat{o}$ are, as the state vectors, abstracted elements. The states $|x\rangle$ satisfy the improper orthogonality relation

$$\langle x|x'\rangle = \delta_{\sigma\sigma'}\,\delta(\boldsymbol{r}-\boldsymbol{r}') \equiv \delta(x,x') . \tag{B.24}$$

Alternatively one may interpret $\langle x|x'\rangle$ as a wavefunction, the representation of an eigenstate of the position/spin operator in position/spin space. Equation (B.24) then states that the probability to find a particle at any other point in space than its eigenvalue vanishes for eigenstates of $\hat{\boldsymbol{r}}$. Two different wavefunctions $\langle x|x'\rangle$ and $\langle x|x''\rangle$ are orthogonal, as required by their definition as eigenstates of $\hat{\boldsymbol{r}}$ and $\hat{s}_z$,

$$\int dx\,\langle x'|x\rangle\langle x|x''\rangle = \delta(x',x'') = \langle x'|x''\rangle . \tag{B.25}$$

Equation (B.25) also demonstrates that the state vectors $|x\rangle$ are not properly normalizable, so that they are not elements of the Hilbert space $\mathscr{H}_1$. They can nevertheless be used to represent the elements of $\mathscr{H}_1$ in the sense of a basis set expansion, as they form a complete basis in a vector space which contains $\mathscr{H}_1$. An example for such a representation is the Fourier representation of normalizable functions in terms of

[2] These relations are replaced by

$$\langle\alpha|\beta\rangle = S_{\alpha\beta} \qquad \sum_{\alpha\beta} |\alpha\rangle S^{-1}_{\alpha\beta}\langle\beta| = \hat{1}_{\mathscr{H}_1} ,$$

in the case of a non-orthogonal basis. The matrix elements $S^{-1}_{\alpha\beta}$ are elements of the inverse overlap matrix, which is defined by

$$\mathsf{S}\mathsf{S}^{-1} = 1 \qquad \rightarrow \qquad \sum_\beta S_{\alpha\beta}S^{-1}_{\beta\gamma} = \delta_{\alpha\gamma} .$$

non-normalizable plane waves. The completeness relation for the states $|x\rangle$ can be extracted from Eq. (B.25), which is valid for arbitrary $|x'\rangle$, $|x''\rangle$,

$$\int dx\,|x\rangle\langle x| \;\equiv\; \sum_{\sigma}\int d^3r\,|\boldsymbol{r}\sigma\rangle\langle\boldsymbol{r}\sigma| \;=\; \hat{1}\,. \tag{B.26}$$

The quantity $\hat{1}$ stands for the unit operator in the space which contains $\mathscr{H}_1$.

With these basic elements of the Dirac notation the orthogonality and completeness relations of the one particle wavefunctions, (B.4) and (B.5) respectively, can be reproduced in a consistent fashion. The notation also opens access to all formal aspects of quantum mechanics.

In the next step the Dirac notation can be extended to deal with N-particle systems. The N-particle Hilbert space $\mathscr{H}_N$ is spanned by the product states

$$|\alpha_1\cdots\alpha_N) = |\alpha_1\rangle\otimes\cdots\otimes|\alpha_N\rangle\,. \tag{B.27}$$

In these N-particle states the particle k is in the quantum state α_k, i.e. the position of a single-particle state in the tensor product on the right-hand side characterizes a particular particle of the system. It is usual to omit the product sign $\otimes$, when working with the states $|\alpha_1\cdots\alpha_N)$. Nevertheless, the convention associating particle k with position k still applies.

The bra-ket combination of (B.27) with

$$|x_1\cdots x_N) = |x_1\rangle\otimes\cdots\otimes|x_N\rangle \tag{B.28}$$

yields the product wavefunction (B.7),

$$\Phi^{\mathrm{c}}_{\alpha_1\cdots\alpha_N}(x_1\cdots x_N) = (x_1\cdots x_N|\alpha_1\cdots\alpha_N) = \langle x_1|\alpha_1\rangle\cdots\langle x_N|\alpha_N\rangle\,. \tag{B.29}$$

The N-particle states (B.27) constitute a basis of $\mathscr{H}_N$. They form a complete set provided the 1-particle basis is complete,

$$\sum_{\alpha_1\cdots\alpha_N}|\alpha_1\cdots\alpha_N)(\alpha_1\cdots\alpha_N| = \sum_{\alpha_1}|\alpha_1\rangle\langle\alpha_1|\cdots\sum_{\alpha_N}|\alpha_N\rangle\langle\alpha_N| = \hat{1}_{\mathscr{H}_N}\,, \tag{B.30}$$

where $\hat{1}_{\mathscr{H}_N}$ represents the unit operator in $\mathscr{H}_N$. Similarly, one has in the x-representation,

$$\int dx_1\cdots dx_N\,|x_1\cdots x_N)(x_1\cdots x_N| = \hat{1}_N\,, \tag{B.31}$$

where $\hat{1}_N$ is the unit operator of the (N-particle) space which contains $\mathscr{H}_N$.

The fermion and boson sectors of $\mathscr{H}_N$ are defined in the same fashion as before. The fermion sector is spanned by the antisymmetrized states[3]

[3] Many-body states in the form of products will be denoted by $|\cdots)$, antisymmetrized states by $|\cdots\rangle$.

$$|\alpha_1 \cdots \alpha_N\rangle = \frac{1}{\sqrt{N!}} \sum_{P \in S_N} (-1)^P |\alpha_{p_1} \cdots \alpha_{p_N}) = \frac{1}{\sqrt{N!}} \sum_{P \in S_N} (-1)^P |\alpha_{p_1}\rangle \cdots |\alpha_{p_N}\rangle \,. \tag{B.32}$$

In the states $|\alpha_1 \cdots \alpha_N\rangle$ the position of the quantum number is no longer related to a particular particle. A given particle is not in a particular single-particle state. The individual terms on the right-hand side of (B.32) are, however, product states of the form (B.27), so that the position k in the product characterizes a particular particle.

The N-fermion wavefunction (B.11) is given by the bra-ket combination

$$\begin{aligned}(x_1 \cdots x_N|\alpha_1 \cdots \alpha_N\rangle &= \frac{1}{\sqrt{N!}} \sum_{P \in S_N} (-1)^P (x_1 \cdots x_N|\alpha_{p_1} \cdots \alpha_{p_N}) \\ &= \frac{1}{\sqrt{N!}} \sum_{P \in S_N} (-1)^P \langle x_1|\alpha_{p_1}\rangle \cdots \langle x_N|\alpha_{p_N}\rangle \\ &= \frac{1}{\sqrt{N!}} \sum_{P \in S_N} (-1)^P \langle x_{p_1}|\alpha_1\rangle \cdots \langle x_{p_N}|\alpha_N\rangle \,. \end{aligned} \tag{B.33}$$

Note, that only one of the state vectors in the bra-ket scalar product is an antisymmetrized state, either the bra or the ket vector,

$$\Phi_{\alpha_1 \cdots \alpha_N}(x_1 \cdots x_N) = \langle x_1 \cdots x_N|\alpha_1 \cdots \alpha_N) = (x_1 \cdots x_N|\alpha_1 \cdots \alpha_N\rangle \,. \tag{B.34}$$

The other is a simple product state.

The antisymmetric N-fermion state vectors satisfy the orthonormality relation (B.12),

$$\langle \alpha_1 \cdots \alpha_N|\beta_1 \cdots \beta_N\rangle = \sum_{P \in S_N} (-1)^P \delta_{\alpha_1 \beta_{p_1}} \cdots \delta_{\alpha_N \beta_{p_N}} \,, \tag{B.35}$$

which may be verified by insertion of (B.32) and subsequent use of (B.21) for the individual particles. As a single-particle state can at most be occupied by one fermion, at most one of the possible permutations of the single-particle overlap matrices can be non-zero. If the state labels are arranged in a strict order, $\alpha_1 < \cdots < \alpha_N$, the result can be written as

$$\langle \alpha_1 \cdots \alpha_N|\beta_1 \cdots \beta_N\rangle = \delta_{\alpha_1 \beta_1} \cdots \delta_{\alpha_N \beta_N} \,. \tag{B.36}$$

Similarly, the completeness relations (B.17) and (B.18) have the form

$$\frac{1}{N!} \sum_{\alpha_1 \cdots \alpha_N} |\alpha_1 \cdots \alpha_N\rangle\langle \alpha_1 \cdots \alpha_N| = \hat{1}_{\mathscr{F}_N} \tag{B.37}$$

$$\sum_{\alpha_1 < \alpha_2 \cdots < \alpha_N} |\alpha_1 \cdots \alpha_N\rangle\langle \alpha_1 \cdots \alpha_N| = \hat{1}_{\mathscr{F}_N} \,. \tag{B.38}$$

B.2 Fock Space

There are several reasons to combine the Hilbert spaces for all possible particle numbers into a more general space, the *Fock space*. Particle numbers of a particular species are not necessarily conserved in quantum processes or there might be the need to describe a thermodynamical equilibrium without a fixed number of particles. The Fock space of fermions $\mathscr{F}$ is defined as the direct sum of the N-fermions spaces $\mathscr{F}_N$ for all particle numbers,

$$\mathscr{F} = \mathscr{F}_0 \oplus \mathscr{F}_1 \oplus \cdots \oplus \mathscr{F}_N \oplus \cdots . \tag{B.39}$$

In addition to the well-defined spaces $\mathscr{F}_N$, it includes a sector $\mathscr{F}_0$ containing no particle at all. The only state in $\mathscr{F}_0$ is the so-called *vacuum state*

$$|0\rangle \qquad \text{with} \qquad \langle 0|0\rangle = 1 . \tag{B.40}$$

The actual specification of this state requires the application of the creation and annihilation operators, which will be detailed in the next section. A complete and orthonormal basis of $\mathscr{F}$ is obtained by combining all N-fermion basis sets with $|0\rangle\langle 0|$, so that the completeness relation in $\mathscr{F}$ reads

$$|0\rangle\langle 0| + \sum_{N=1}^{\infty} \frac{1}{N!} \sum_{\alpha_1 \cdots \alpha_N} |\alpha_1 \cdots \alpha_N\rangle\langle \alpha_1 \cdots \alpha_N| = \hat{1}_{\mathscr{F}} . \tag{B.41}$$

B.2.1 Creation and Annihilation Operators

The action of a fermion creation operator $\hat{a}^\dagger_\alpha$ on a N-fermion basis state generates an $(N+1)$-fermion basis state

$$\hat{a}^\dagger_\alpha |\alpha_1 \cdots \alpha_N\rangle := |\alpha\, \alpha_1 \cdots \alpha_N\rangle . \tag{B.42}$$

The $(N+1)$-fermion state is properly normalized and antisymmetrized. The definition (B.42) of the operators $\hat{a}^\dagger_\alpha$ is unambiguous, as all states involved are well-defined. Extension of Eq. (B.42) to $N = 0$ defines the vacuum state as the state from which $\hat{a}^\dagger_\alpha$ generates the single-particle state $|\alpha\rangle$,

$$\hat{a}^\dagger_\alpha |0\rangle = |\alpha\rangle . \tag{B.43}$$

Combination of the definitions (B.42) and (B.43) allows a representation of any N-fermion basis state in terms of creation operators and the vacuum,

$$|\alpha_1 \cdots \alpha_N\rangle = \hat{a}^\dagger_{\alpha_1} \cdots \hat{a}^\dagger_{\alpha_N} |0\rangle . \tag{B.44}$$

The entire basis of Fock space can be generated by the repeated action of creation operators on the vacuum state.

The associated annihilation operator $\hat{a}_\alpha$ is defined by hermitian conjugation of $\hat{a}^\dagger_\alpha$

$$\hat{a}_\alpha := \left(\hat{a}^\dagger_\alpha\right)^\dagger \,. \tag{B.45}$$

Consequently one has

$$\begin{aligned} \langle\alpha_1| &= \langle 0|\,\hat{a}_{\alpha_1} \\ \langle\alpha_1\,\alpha_2\cdots\alpha_N| &= \langle\alpha_2\cdots\alpha_N|\,\hat{a}_{\alpha_1} = \langle 0|\,\hat{a}_{\alpha_N}\cdots\hat{a}_{\alpha_1}\,. \end{aligned}$$

The antisymmetry of fermion states of the form (B.44) is incorporated by demanding specific commutation relations for the creation operators. With the interchange of two quantum numbers in (B.44) one arrives at

$$\begin{aligned} |\alpha_1\,\alpha_2\,\alpha_3\cdots\alpha_N\rangle &= \hat{a}^\dagger_{\alpha_1}\hat{a}^\dagger_{\alpha_2}\hat{a}^\dagger_{\alpha_3}\cdots\hat{a}^\dagger_{\alpha_N}|0\rangle \\ &= -|\alpha_2\,\alpha_1\,\alpha_3\cdots\alpha_N\rangle \\ &= -\hat{a}^\dagger_{\alpha_2}\hat{a}^\dagger_{\alpha_1}\hat{a}^\dagger_{\alpha_3}\cdots\hat{a}^\dagger_{\alpha_N}|0\rangle\,. \end{aligned} \tag{B.46}$$

This relation requires that the creation operators (and hence the annihilation operators) satisfy *anticommutation relations*,

$$\left\{\hat{a}^\dagger_\alpha,\hat{a}^\dagger_\beta\right\} \;=\; \left\{\hat{a}_\alpha,\hat{a}_\beta\right\} \;=\; 0 \qquad \text{with} \quad \left\{\hat{A},\hat{B}\right\} = \hat{A}\hat{B}+\hat{B}\hat{A}\,, \tag{B.47}$$

as (B.46) must hold for arbitrary states $|\alpha_3,\ldots\alpha_N\rangle$.

The commutation relation between creation and annihilation operators can be derived in the following fashion: as first step consider the expectation value of an annihilation operator for arbitrary basis set states,

$$\langle\alpha_1\cdots\alpha_M|\hat{a}_\mu|\beta_1\cdots\beta_N\rangle = \langle\mu\,\alpha_1\cdots\alpha_M|\beta_1\cdots\beta_N\rangle\,. \tag{B.48}$$

The right-hand side of (B.48) necessarily vanishes if $M+1\neq N$, irrespective of the values of the quantum numbers involved. This shows that the state $\hat{a}_\mu|\beta_1\cdots\beta_N\rangle$ is a $(N-1)$-particle state—the operator $\hat{a}_\mu$ annihilates one particle. In particular, the expression $\langle 0|\hat{a}_\mu|0\rangle = 0$ requires

$$\hat{a}_\mu|0\rangle = 0 \qquad \left(\text{similarly, } \langle 0|\hat{a}^\dagger_\mu = 0\right)\,. \tag{B.49}$$

Particles can not be destroyed, if there are no particles.

The next step is an investigation of the action of the annihilation operator on an arbitrary basis state. With the completeness relation (B.41) one obtains

$$\begin{aligned}\hat{a}_\mu|\beta_1\cdots\beta_N\rangle &= \sum_{M=1}^{\infty}\frac{1}{M!}\sum_{\alpha_1\cdots\alpha_M}|\alpha_1\cdots\alpha_M\rangle\langle\alpha_1\cdots\alpha_M|\hat{a}_\mu|\beta_1\cdots\beta_N\rangle \\ &= \sum_{M=1}^{\infty}\frac{1}{M!}\sum_{\alpha_1\cdots\alpha_M}\langle\mu\,\alpha_1\cdots\alpha_M|\beta_1\cdots\beta_N\rangle\,|\alpha_1\cdots\alpha_M\rangle \\ &= \frac{1}{(N-1)!}\sum_{\alpha_1\cdots\alpha_{N-1}}\langle\mu\,\alpha_1\cdots\alpha_{N-1}|\beta_1\cdots\beta_N\rangle\,|\alpha_1\cdots\alpha_{N-1}\rangle\,.\end{aligned}$$

The last line can be processed further with the orthonormality relation (B.35),

$$\begin{aligned}&\hat{a}_\mu|\beta_1\cdots\beta_N\rangle \\ &= \frac{1}{(N-1)!}\sum_{\alpha_1\cdots\alpha_{N-1}}\sum_{P\in S_N}(-1)^P\delta_{\mu\beta_{p_1}}\,\delta_{\alpha_1\beta_{p_2}}\cdots\delta_{\alpha_{N-1}\beta_{p_N}}|\alpha_1\cdots\alpha_{N-1}\rangle \\ &= \frac{1}{(N-1)!}\sum_{P\in S_N}(-1)^P\delta_{\mu\beta_{p_1}}|\beta_{p_2}\cdots\beta_{p_N}\rangle\,.\end{aligned}$$

The sum over the $N!$ permutations P can be written more explicitly in terms of an expansion with respect to the entry with the index i as

$$\hat{a}_\mu|\beta_1\cdots\beta_N\rangle = \frac{1}{(N-1)!}\sum_{i=1}^{N}(-1)^{i-1}\delta_{\mu\beta_i}\sum_{P'\in S_{N-1}}(-1)^{P'}|\beta_{p'_1}\cdots\not{\beta}_i\cdots\beta_{p'_N}\rangle\,.$$

The sum over the permutations P' of the numbers $1,\ldots,i-1,i+1,\ldots N$ (the omission of i is indicated by $\not{\beta}_i$) represents $(N-1)!$ times the same $(N-1)$-particle state

$$|\beta_1\cdots\beta_{i-1}\,\beta_{i+1}\cdots\beta_N\rangle = \frac{1}{(N-1)!}\sum_{P'\in S_{N-1}}(-1)^{P'}|\beta_{p'_1}\cdots\not{\beta}_i\cdots\beta_{p'_N}\rangle\,.$$

The final result

$$\hat{a}_\mu|\beta_1\cdots\beta_N\rangle = \sum_{i=1}^{N}(-1)^{i-1}\delta_{\mu\beta_i}|\beta_1\cdots\beta_{i-1}\,\beta_{i+1}\cdots\beta_N\rangle \tag{B.50}$$

shows: the right-hand is only non-zero, if the quantum number μ is identical with one of the β_i,

$$\hat{a}_\mu|\beta_1\cdots\beta_N\rangle = \begin{cases}(-1)^{i-1}|\beta_1\cdots\beta_{i-1}\,\beta_{i+1}\cdots\beta_N\rangle & \text{if } \mu=\beta_i \\ 0 & \text{otherwise}\end{cases}\,. \tag{B.51}$$

Combination of (B.50) with (B.42) then yields

$$\begin{aligned}\hat{a}_\mu\hat{a}^\dagger_\nu|\alpha_1\cdots\alpha_N\rangle &= \delta_{\mu\nu}|\alpha_1\cdots\alpha_N\rangle \\ &\quad+\sum_{i=1}^{N}(-1)^i\delta_{\mu\alpha_i}|\nu\alpha_1\cdots\alpha_{i-1}\,\alpha_{i+1}\cdots\alpha_N\rangle\,,\end{aligned} \tag{B.52}$$

as well as

$$\hat{a}_\nu^\dagger \hat{a}_\mu |\alpha_1 \cdots \alpha_N\rangle = \sum_{i=1}^{N} (-1)^{i-1} \delta_{\mu\alpha_i} |\nu\alpha_1 \cdots \alpha_{i-1}\, \alpha_{i+1} \cdots \alpha_N\rangle \,. \tag{B.53}$$

Both relations are valid for arbitrary $|\alpha_1 \cdots \alpha_N\rangle$, so that one can extract the anti-commutation relation

$$\left\{\hat{a}_\mu, \hat{a}_\nu^\dagger\right\} = \delta_{\mu\nu} \,. \tag{B.54}$$

With Eqs. (B.42)–(B.50) and (B.54) the set of basic relations for creation and annihilation operators is complete. *All* operations and manipulations in Fock space can be handled with these tools.

The creation or destruction of a particle has so far been associated with a basis labelled by an index α. A transition to an alternative basis can be achieved with the aid of completeness relations. For example, the relations (B.21) and (B.26) can be used to write down the identities (valid for any kind of particle)

$$|\alpha\rangle = \int dx\, |x\rangle\langle x|\alpha\rangle \;=\; \int dx\, \phi_\alpha(x) |x\rangle \tag{B.55}$$

$$|x\rangle = \sum_\alpha |\alpha\rangle\langle\alpha\, |x\rangle \;=\; \sum_\alpha \phi_\alpha^*(x)\, |\alpha\rangle \,, \tag{B.56}$$

which can be interpreted as a unitary basis transformation in $\mathscr{H}_1$. The second of these relations suggests the introduction of the operators $\hat{\psi}(x)$ and $\hat{\psi}^\dagger(x)$ with

$$|x\rangle = \hat{\psi}^\dagger(x)|0\rangle \qquad \text{and} \qquad \langle x| = \langle 0|\, \hat{\psi}(x) \,. \tag{B.57}$$

These operators describe the creation and the destruction of a particle at the "position x". For this reason they are usually referred to as *field operators*. In other words: the basis transformations (B.55) and (B.56) induce a corresponding transformation between the associated creation and annihilation operators,

$$\hat{\psi}^\dagger(x) = \sum_\alpha \phi_\alpha^*(x)\, \hat{a}_\alpha^\dagger \;=\; \sum_\alpha \langle\alpha|x\rangle\, \hat{a}_\alpha^\dagger \tag{B.58}$$

$$\hat{\psi}(x) = \sum_\alpha \phi_\alpha(x) \hat{a}_\alpha \;=\; \sum_\alpha \langle x|\alpha\rangle \hat{a}_\alpha \,, \tag{B.59}$$

with the inverse transformation

$$\hat{a}_\alpha = \int dx\, \phi_\alpha^*(x)\, \hat{\psi}(x) \tag{B.60}$$

$$\hat{a}_\alpha^\dagger = \int dx\, \phi_\alpha(x)\, \hat{\psi}^\dagger(x) \,. \tag{B.61}$$

The relations (B.58), (B.59) indicate directly that the field operators are objects with two components in the case of spin 1/2 fermions,

$$\hat{\psi}(x) = \hat{\psi}(\boldsymbol{r}\sigma) = \begin{cases} \hat{\psi}(\boldsymbol{r}, +\frac{1}{2}) \text{ if } \sigma = +\frac{1}{2} \\ \hat{\psi}(\boldsymbol{r}, -\frac{1}{2}) \text{ if } \sigma = -\frac{1}{2} \end{cases} . \tag{B.62}$$

The anticommutation relations (B.54) and (B.47) and the transformations (B.58)–(B.61) can only be consistent, if the field operators satisfy

$$\left\{\hat{\psi}(x), \hat{\psi}^{\dagger}(x')\right\} = \delta(x,x') \tag{B.63}$$

$$\left\{\hat{\psi}(x), \hat{\psi}(x')\right\} = \left\{\hat{\psi}^{\dagger}(x), \hat{\psi}^{\dagger}(x')\right\} = 0 . \tag{B.64}$$

The structure of the commutation relations is conserved under basis transformations. A transformation between the basis $|\alpha\rangle$ and any other (single-particle) basis proceeds in the same fashion.

B.2.2 1-Particle Operators

The Pauli principle requires that quantum particles are indistinguishable. Observables of many particle systems can, as a consequence, only be represented by operators which are symmetric under exchange of particles.

An important class of operators in N-particle space are those constructed by summation over terms acting on a single particle,

$$\hat{F} = \sum_{i=1}^{N} \hat{f}_i . \tag{B.65}$$

They are referred to as 1-particle (or single-particle) operators. More correctly they might be called 1-particle operators in an N-particle system. A second important type of operators is constructed by summation of terms linking two particles,

$$\hat{W} = \sum_{i,j=1;\, i<j}^{N} \hat{w}_{ij} . \tag{B.66}$$

These operators are therefore called 2-particle operators.

A 1-particle operator $\hat{f}$ can be specified in the x-, the α- or any other representation. In the Dirac notation one obtains for instance for the operator of the kinetic energy of a single particle in the x-representation

$$\langle x|\hat{t}|x'\rangle = \delta(x,x') \frac{(-i\hbar\boldsymbol{\nabla}')^2}{2m} . \tag{B.67}$$

The α- and the x-representation of an operator $\hat{f}$ can be related with the aid of the completeness relation

$$\langle\alpha|\hat{f}|\beta\rangle = \int dx\, dx' \, \langle\alpha|x'\rangle\langle x'|\hat{f}|x\rangle\langle x|\beta\rangle . \tag{B.68}$$

The action of $\hat{f}$ on a 1-particle state $|\gamma\rangle$ can also be rewritten with the completeness relation as

$$\hat{f}|\gamma\rangle = \sum_{\alpha} |\alpha\rangle\langle\alpha|\hat{f}|\gamma\rangle \; . \tag{B.69}$$

This implies that the representation of a 1-particle operator in terms of creation and annihilation operators must have the form

$$\hat{f} = \sum_{\alpha\beta} \langle\alpha|\hat{f}|\beta\rangle \, \hat{a}^{\dagger}_{\alpha}\hat{a}_{\beta} \; . \tag{B.70}$$

The operators $\hat{a}^{\dagger}_{\alpha}$ and $\hat{a}_{\beta}$ are specified in terms of the single-particle basis to which $|\gamma\rangle$ belongs. Equation (B.70) can be verified by insertion,

$$\hat{f}|\gamma\rangle = \sum_{\alpha\beta} \langle\alpha|\hat{f}|\beta\rangle \, \hat{a}^{\dagger}_{\alpha}\hat{a}_{\beta}\hat{a}^{\dagger}_{\gamma}|0\rangle = \sum_{\alpha} \langle\alpha|\hat{f}|\gamma\rangle \, \hat{a}^{\dagger}_{\alpha}|0\rangle \; , \tag{B.71}$$

and comparison with Eq. (B.69).

The 1-particle operator $\hat{F} = \sum_i \hat{f}_i$ in Fock space is completely characterized by the action of $\hat{f}$ within the 1-particle segment of this space. It follows that the operator (B.70) can also serve as a representation of the operator $\hat{F}$,

$$\hat{F} = \sum_{\alpha\beta} \langle\alpha|\hat{f}|\beta\rangle \, \hat{a}^{\dagger}_{\alpha}\hat{a}_{\beta} \; . \tag{B.72}$$

Due to the combination $\hat{a}^{\dagger}_{\alpha}\hat{a}_{\beta}$ the operator only connects states of the same segment of Fock space. In order to evaluate the action of this operator on a N-particle state one may use the commutation relation

$$\left[\hat{F}, \hat{a}^{\dagger}_{\alpha}\right] = \sum_{\beta\gamma} \langle\beta|\hat{f}|\gamma\rangle \left[\hat{a}^{\dagger}_{\beta}\hat{a}_{\gamma}, \hat{a}^{\dagger}_{\alpha}\right] = \sum_{\beta} \langle\beta|\hat{f}|\alpha\rangle \hat{a}^{\dagger}_{\beta} \; . \tag{B.73}$$

Use of (B.73) allows a direct evaluation of $\hat{F}|\alpha_1 \cdots \alpha_N\rangle$ as soon as $[\hat{F}, \hat{a}^{\dagger}_{\alpha}]$ is introduced by suitable addition and subtraction of terms,

$$\begin{aligned} \hat{F}\,\hat{a}^{\dagger}_{\alpha_1}\cdots\hat{a}^{\dagger}_{\alpha_N}|0\rangle = {} & [\hat{F}, \hat{a}^{\dagger}_{\alpha_1}]\,\hat{a}^{\dagger}_{\alpha_2}\cdots\hat{a}^{\dagger}_{\alpha_N}|0\rangle + \hat{a}^{\dagger}_{\alpha_1}\,[\hat{F}, \hat{a}^{\dagger}_{\alpha_2}]\,\hat{a}^{\dagger}_{\alpha_3}\cdots\hat{a}^{\dagger}_{\alpha_N}|0\rangle \\ & + \cdots + \hat{a}^{\dagger}_{\alpha_1}\cdots\hat{a}^{\dagger}_{\alpha_{(N-1)}}\,[\hat{F}, \hat{a}^{\dagger}_{\alpha_N}]\,|0\rangle \, . \end{aligned} \tag{B.74}$$

After replacement of the commutator one obtains

$$\begin{aligned} = {} & \sum_{\beta_1} \langle\beta_1|\hat{f}|\alpha_1\rangle \, \hat{a}^{\dagger}_{\beta_1}\hat{a}^{\dagger}_{\alpha_2}\cdots\hat{a}^{\dagger}_{\alpha_N}|0\rangle + \sum_{\beta_2} \langle\beta_2|\hat{f}|\alpha_2\rangle \, \hat{a}^{\dagger}_{\alpha_1}\hat{a}^{\dagger}_{\beta_2}\hat{a}^{\dagger}_{\alpha_3}\cdots\hat{a}^{\dagger}_{\alpha_N}|0\rangle \\ & + \cdots + \sum_{\beta_N} \langle\beta_N|\hat{f}|\alpha_N\rangle \, \hat{a}^{\dagger}_{\alpha_1}\cdots\hat{a}^{\dagger}_{\alpha_{N-1}}\hat{a}^{\dagger}_{\beta_N}|0\rangle \; . \end{aligned} \tag{B.75}$$

This explicit result can be written in the compact form

$$\hat{F}|\alpha_1 \cdots \alpha_N\rangle = \sum_{i=1}^{N} \sum_{\beta_i} \langle \beta_i|\hat{f}|\alpha_i\rangle \, \hat{a}^\dagger_{\alpha_1} \cdots \hat{a}^\dagger_{\beta_i} \cdots \hat{a}^\dagger_{\alpha_N}|0\rangle \, . \tag{B.76}$$

The notation indicates that $\hat{a}^\dagger_{\beta_i}$ stands at position i in the sequence of creation operators. Each of the particles is transferred with a certain probability, determined by the matrix element $\langle \beta_i|\hat{f}|\alpha_i\rangle$, into a single-particle state which is not already present in $|\alpha_1 \cdots \alpha_N\rangle$. The result (B.75) can also be used to evaluate the only non-vanishing matrix elements of $\hat{F}$,

$$\langle \alpha_1 \cdots \alpha_N|\hat{F}|\alpha_1 \cdots \alpha_N\rangle = \sum_{i=1} \langle \alpha_i|\hat{f}|\alpha_i\rangle \tag{B.77}$$

$$\langle \alpha_1 \cdots \beta_k \cdots \alpha_N|\hat{F}|\alpha_1 \cdots \alpha_N\rangle = \langle \beta_k|\hat{f}|\alpha_k\rangle \, . \tag{B.78}$$

The label $\beta_k \neq \alpha_i, \; i = 1, \ldots N$ replaces α_k in the bra-state of Eq. (B.78). 1-particle operators can only connect states of Fock space with the same number of particles, which differ at most in one occupation.

The operator (B.72) in the second quantized representation can alternatively be written in terms of the field operators

$$\begin{aligned} \hat{F} &= \sum_{\alpha\beta} \langle \alpha|\hat{f}|\beta\rangle \hat{a}^\dagger_\alpha \hat{a}_\beta \; = \; \int dx dx' \sum_{\alpha\beta} \langle \alpha|x'\rangle \langle x'|\hat{f}|x\rangle \langle x|\beta\rangle \hat{a}^\dagger_\alpha \hat{a}_\beta \\ &= \int dx dx' \, \hat{\psi}^\dagger(x') \langle x'|\hat{f}|x\rangle \hat{\psi}(x) \, , \end{aligned} \tag{B.79}$$

or, for that matter, in terms of any other basis, which is related by a unitary transformation, as e.g.

$$\hat{b}^\dagger_k = \sum_\alpha C_{k,\alpha} \hat{a}^\dagger_\alpha \qquad \hat{b}_k = \sum_\alpha C^*_{k,\alpha} \hat{a}_\alpha \tag{B.80}$$

with the inverse

$$\hat{a}^\dagger_\alpha = \sum_k C^*_{k,\alpha} b^\dagger_k \qquad \hat{a}_\alpha = \sum_k C_{k,\alpha} \hat{b}_k \, . \tag{B.81}$$

In the basis with the creation and annihilation operators $\hat{b}_k, \hat{b}^\dagger_k$ one obtains

$$\hat{F} = \sum_{k_1,k_2} \langle k_1|\hat{f}|k_2\rangle \, \hat{b}^\dagger_{k_1} \hat{b}_{k_2} \, . \tag{B.82}$$

The form of the representation is independent of the basis chosen.

B.2.3 2-Particle Operators

Similar statements can be made for 2-particle operators, though detailed calculations and proofs are more involved. These operators are characterized by matrix elements in the 2-particle sector of the Fock space, e.g. in the x-representation by

$$(x_1' x_2' | \hat{w} | x_1 x_2) \; .$$

The notation indicates that the matrix element under consideration is the canonical matrix element, obtained with the product states of the 2-particle Hilbert space. One example is the interaction between two particles, which is usually local with respect to the coordinates of the two particles involved,

$$(x_1' x_2' | \hat{w} | x_1 x_2) = \delta(x_1, x_1') \, \delta(x_2, x_2') \, w(x_1, x_2) \; . \tag{B.83}$$

The function $w(x_1, x_2)$ has to be symmetric and real, as

- the corresponding force has to satisfy Newton's third axiom, and
- the operator $\hat{w}$ has to be hermitian.

It may either be spin-dependent, or not,

$$w(x_1, x_2) = w(\boldsymbol{r}_1, \boldsymbol{r}_2) \; . \tag{B.84}$$

Equation (B.84) applies in particular to the Coulomb interaction, which is of primary interest in the present context. In fact, the Coulomb force is a good example for an interaction which is, in addition, Galilei invariant. The function $w(\boldsymbol{r}_1, \boldsymbol{r}_2)$ depends only on the difference of the position vectors in this case

$$w(\boldsymbol{r}_1, \boldsymbol{r}_2) = w(\boldsymbol{r}_1 - \boldsymbol{r}_2) \; . \tag{B.85}$$

The α-representation of the two-body interaction is again obtained with the aid of the completeness relation,

$$(\beta_1 \beta_2 | \hat{w} | \alpha_1 \alpha_2) = \int dx_1' dx_2' dx_1 dx_2 \; (\beta_1 \beta_2 | x_1' x_2')(x_1' x_2' | \hat{w} | x_1 x_2)(x_1 x_2 | \alpha_1 \alpha_2) \; , \tag{B.86}$$

in detail for the case (B.83),

$$(\beta_1 \beta_2 | \hat{w} | \alpha_1 \alpha_2) = \int dx_1 dx_2 \; \phi_{\beta_1}^*(x_1) \phi_{\beta_2}^*(x_2) w(x_1, x_2) \phi_{\alpha_1}(x_1) \phi_{\alpha_2}(x_2) \; . \tag{B.87}$$

The order of the quantum labels in the 2-particle bra- and ket-states is, as indicated explicitly in (B.87), of relevance. The first label in the bra- and in the ket-state is associated with the coordinate x_1, the second with x_2. The matrix element satisfies the symmetry relations

$$(\beta_1 \beta_2 | \hat{w} | \alpha_1 \alpha_2) = (\beta_2 \beta_1 | \hat{w} | \alpha_2 \alpha_1) = (\alpha_1 \alpha_2 | \hat{w} | \beta_1 \beta_2)^* \; . \tag{B.88}$$

The action of a 2-particle operator on antisymmetric 2-particle states can be reformulated with the aid of the completeness relation (B.37),

$$\hat{w}|\alpha_1\alpha_2\rangle = \frac{1}{2!}\sum_{\beta_1\beta_2}\langle\beta_1\beta_2|\hat{w}|\alpha_1\alpha_2\rangle|\,\beta_1\beta_2\rangle\,. \tag{B.89}$$

The matrix element in (B.89) is the *antisymmetric* matrix element, which can be expressed in terms of canonical matrix elements by use of Eq. (B.32),

$$\begin{aligned}\langle\beta_1\beta_2|\hat{w}|\alpha_1\alpha_2\rangle &= \frac{1}{2}\big\{(\beta_1\beta_2| - (\beta_2\beta_1|\,\big\}\hat{w}\big\{|\alpha_1\alpha_2) - |\alpha_2\alpha_1)\big\}\\ &= (\beta_1\beta_2|\hat{w}|\alpha_1\alpha_2) - (\beta_1\beta_2|\hat{w}|\alpha_2\alpha_1)\,.\end{aligned} \tag{B.90}$$

The second line in Eq. (B.90) follows from the symmetry of the interaction against the interchange of the two particles. The properties of this matrix element,

$$\begin{aligned}\langle\beta_1\beta_2|\hat{w}|\alpha_1\alpha_2\rangle &= -\langle\beta_2\beta_1|\hat{w}|\alpha_1\alpha_2\rangle \;=\; -\langle\beta_1\beta_2|\hat{w}|\alpha_2\alpha_1\rangle\\ &= \langle\beta_2\beta_1|\hat{w}|\alpha_2\alpha_1\rangle \;=\; \langle\alpha_1\alpha_2|\hat{w}|\beta_1\beta_2\rangle^*\,,\end{aligned} \tag{B.91}$$

follow directly from the definition and the properties (B.88) of the direct matrix elements involved. Combination of Eqs. (B.88)–(B.91) yields the alternative form

$$\hat{w}|\alpha_1\alpha_2\rangle = \sum_{\beta_1\beta_2}(\beta_1\beta_2|\hat{w}|\alpha_1\alpha_2)\,|\beta_1\beta_2\rangle\,. \tag{B.92}$$

The second quantized form of a 2-particle operator in Fock space that reproduces (B.92) is

$$\hat{W} = \frac{1}{2}\sum_{\alpha\beta\gamma\delta}(\alpha\beta|\hat{w}|\gamma\delta)\,\hat{a}^\dagger_\alpha a^\dagger_\beta\hat{a}_\delta\hat{a}_\gamma\,. \tag{B.93}$$

One should take note of the sequence of the labels of the operators with respect to the sequence of the labels of the states. The calculation of the action of this operator on a 2-particle state of fermion Fock space involves the evaluation of

$$\hat{W}|\alpha_1\alpha_2\rangle = \frac{1}{2}\sum_{\beta_1\beta_2\gamma_1\gamma_2}(\beta_1\beta_2|\hat{w}|\gamma_1\gamma_2)\,\hat{a}^\dagger_{\beta_1}\hat{a}^\dagger_{\beta_2}\hat{a}_{\gamma_2}\hat{a}_{\gamma_1}\hat{a}^\dagger_{\alpha_1}\hat{a}^\dagger_{\alpha_2}|0\rangle\,. \tag{B.94}$$

Rearrangement of the creation and annihilation operators,

$$\hat{a}^\dagger_{\beta_1}\hat{a}^\dagger_{\beta_2}\hat{a}_{\gamma_2}\hat{a}_{\gamma_1}\hat{a}^\dagger_{\alpha_1}\hat{a}^\dagger_{\alpha_2}|0\rangle = (\delta_{\alpha_1\gamma_1}\delta_{\alpha_2\gamma_2} - \delta_{\alpha_1\gamma_2}\delta_{\alpha_2\gamma_1})\,\hat{a}^\dagger_{\beta_1}\hat{a}^\dagger_{\beta_2}|0\rangle \tag{B.95}$$

leads, with (B.91), to the same result as (B.92), namely

$$\hat{W}|\alpha_1\alpha_2\rangle = \sum_{\beta_1\beta_2}(\beta_1\beta_2|\hat{w}|\alpha_1\alpha_2)\,|\beta_1\beta_2\rangle\,. \tag{B.96}$$

The evaluation of the action of the operator $\hat{W}$ on a N-particle state also relies on the use of a suitable commutator,

$$\left[\hat{W},\hat{a}^\dagger_\alpha\right] = \sum_{\beta_1\beta_2\alpha_2} (\beta_1\beta_2|\hat{w}|\alpha\alpha_2)\,\hat{a}^\dagger_{\beta_1}\hat{a}^\dagger_{\beta_2}\hat{a}_{\alpha_2}\,. \tag{B.97}$$

Consequent permutation of the commutator through the string of creation operators of the N-particle state yields

$$\begin{aligned}
&\hat{W}|\alpha_1\cdots\alpha_N\rangle \\
&= \sum_{i=1}^{N} \hat{a}^\dagger_{\alpha_1}\cdots\left[\hat{W},\hat{a}^\dagger_{\alpha_i}\right]\cdots\hat{a}^\dagger_{\alpha_N}|0\rangle \\
&= \sum_{i=1}^{N-1}\sum_{\beta_1\beta_2\gamma_2} (\beta_1\beta_2|\hat{w}|\alpha_i\gamma_2)\,\hat{a}^\dagger_{\alpha_1}\cdots\hat{a}^\dagger_{\alpha_{i-1}}\hat{a}^\dagger_{\beta_1}\hat{a}^\dagger_{\beta_2}\hat{a}_{\gamma_2}\hat{a}^\dagger_{\alpha_{i+1}}\cdots\hat{a}^\dagger_{\alpha_N}|0\rangle\,.
\end{aligned} \tag{B.98}$$

The expression $\hat{a}^\dagger_{\beta_1}\hat{a}^\dagger_{\beta_2}\hat{a}_{\gamma_2}$ stands exactly at the position of $\hat{a}^\dagger_{\alpha_i}$ (the contribution with $i = N$ has been omitted, as it vanishes). The pair $\hat{a}^\dagger_{\beta_2}\hat{a}_{\gamma_2}$ now has to be commuted through the chain of operators to its right,

$$\begin{aligned}
\hat{W}|\alpha_1\cdots\alpha_N\rangle = \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\sum_{\beta_1\beta_2} &(\beta_1\beta_2|\hat{w}|\alpha_i\alpha_j) \\
&\times\hat{a}^\dagger_{\alpha_1}\cdots\hat{a}^\dagger_{\alpha_{i-1}}\hat{a}^\dagger_{\beta_1}\hat{a}^\dagger_{\alpha_{i+1}}\cdots\hat{a}^\dagger_{\alpha_{j-1}}\hat{a}^\dagger_{\beta_2}\hat{a}^\dagger_{\alpha_{j+1}}\cdots\hat{a}^\dagger_{\alpha_N}|0\rangle\,.
\end{aligned} \tag{B.99}$$

This expression can be symmetrized with respect to i and j by use of

$$\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} A_{ij} = \sum_{j=2}^{N}\sum_{i=1}^{j-1} A_{ij}$$

and subsequent simultaneous relabelling $i \leftrightarrow j$, $\beta_1 \leftrightarrow \beta_2$ in half of the right-hand side,

$$\begin{aligned}
\hat{W}|\alpha_1\cdots\alpha_N\rangle = \frac{1}{2}\sum_{i,j=1;i\neq j}^{N}\sum_{\beta_1\beta_2} &(\beta_1\beta_2|\hat{w}|\alpha_i\alpha_j) \\
&\times\hat{a}^\dagger_{\alpha_1}\cdots\hat{a}^\dagger_{\alpha_{i-1}}\hat{a}^\dagger_{\beta_1}\hat{a}^\dagger_{\alpha_{i+1}}\cdots\hat{a}^\dagger_{\alpha_{j-1}}\hat{a}^\dagger_{\beta_2}\hat{a}^\dagger_{\alpha_{j+1}}\cdots\hat{a}^\dagger_{\alpha_N}|0\rangle\,.
\end{aligned}$$

The canonical matrix element can be replaced by its antisymmetric counterpart by using the commutation relations to interchange the positions of $\hat{a}^\dagger_{\beta_1}$ and $\hat{a}^\dagger_{\beta_2}$ in the sequence of creation operators,

$$\begin{aligned}
\hat{W}|\alpha_1\cdots\alpha_N\rangle = \frac{1}{4}\sum_{i,j=1;i\neq j}^{N}\sum_{\beta_1\beta_2} &\langle\beta_1\beta_2|\hat{w}|\alpha_i\alpha_j\rangle \\
&\times\hat{a}^\dagger_{\alpha_1}\cdots\hat{a}^\dagger_{\alpha_{i-1}}\hat{a}^\dagger_{\beta_1}\hat{a}^\dagger_{\alpha_{i+1}}\cdots\hat{a}^\dagger_{\alpha_{j-1}}\hat{a}^\dagger_{\beta_2}\hat{a}^\dagger_{\alpha_{j+1}}\cdots\hat{a}^\dagger_{\alpha_N}|0\rangle\,.
\end{aligned} \tag{B.100}$$

This result shows that at most two of the particles in $|\alpha_1 \cdots \alpha_N\rangle$ are promoted to different single-particle states by application of $\hat{W}$. The matrix elements, which are non-zero, are

- the expectation value,

$$\langle \alpha_1 \cdots \alpha_N | \hat{W} | \alpha_1 \cdots \alpha_N \rangle \;=\; \frac{1}{2} \sum_{i,j=1}^{N} \langle \alpha_i \alpha_j | \hat{w} | \alpha_i \alpha_j \rangle \,, \tag{B.101}$$

- matrix elements with N-particle states, which differ in one quantum number ($\beta_k \neq \alpha_i,\ i = 1 \ldots N$),

$$\langle \alpha_1 \cdots \alpha_{k-1} \beta_k \alpha_{k+1} \cdots \alpha_N | \hat{W} | \alpha_1 \cdots \alpha_k \cdots \alpha_N \rangle = \sum_{i=1}^{N} \langle \beta_k \alpha_i | \hat{w} | \alpha_k \alpha_i \rangle \,, \tag{B.102}$$

- matrix elements with N-particle states, which differ in two quantum numbers ($\beta_k, \beta_l \neq \alpha_i,\ i = 1 \ldots N$),

$$\begin{aligned} &\langle \alpha_1 \cdots \alpha_{k-1} \beta_k \alpha_{k+1} \cdots \alpha_{l-1} \beta_l \alpha_{l+1} \cdots \alpha_N | \hat{W} | \alpha_1 \cdots \alpha_k \cdots \alpha_l \cdots \alpha_N \rangle \\ &= \langle \beta_k \beta_l | \hat{w} | \alpha_k \alpha_l \rangle \end{aligned} \tag{B.103}$$

(with the understanding that β_k stands on position k etc.).

The second quantized form of a 2-particle operator in the x-representation can be obtained from the α-representation with the aid of completeness relation (B.31). Insertion of (B.31) into (B.93) and subsequent use of (B.29) leads to

$$\begin{aligned} \hat{W} &= \frac{1}{2} \sum_{\beta_1 \beta_2 \alpha_1 \alpha_2} \int dx_1 dx_2 \, (\beta_1 \beta_2 | x_1 x_2) w(x_1, x_2) (x_1 x_2 | \alpha_1 \alpha_2) \, \hat{a}^\dagger_{\beta_1} \hat{a}^\dagger_{\beta_2} \hat{a}_{\alpha_2} \hat{a}_{\alpha_1} \\ &= \frac{1}{2} \int dx_1 dx_2 \sum_{\beta_1 \beta_2 \alpha_1 \alpha_2} \phi^*_{\beta_1}(x_1) \phi^*_{\beta_2}(x_2) w(x_1, x_2) \phi_{\alpha_1}(x_1) \phi_{\alpha_2}(x_2) \\ &\qquad \times \hat{a}^\dagger_{\beta_1} \hat{a}^\dagger_{\beta_2} \hat{a}_{\alpha_2} \hat{a}_{\alpha_1} \,. \end{aligned}$$

With Eqs. (B.58), (B.59) one finally obtains

$$\hat{W} \;=\; \frac{1}{2} \int dx_1 dx_2 \, \hat{\psi}^\dagger(x_1) \hat{\psi}^\dagger(x_2) w(x_1, x_2) \hat{\psi}(x_2) \hat{\psi}(x_1) \,. \tag{B.104}$$

Once again, specific attention should be given to the order of the arguments of the annihilation operators.

Appendix C
Scaling Behavior of Many-Body Methods

In order to provide some background for the discussion of the scaling behavior of many-body methods with the basis set size M indicated in the Introduction, we explicitly consider the most relevant expressions which one has to deal with in this Appendix. The analysis is still quite simple for the class of matrix elements, which have to be evaluated in any of the *ab-initio* methods, i.e. the matrix elements of a single-particle operator. Let us thus first consider a multiplicative potential v as the prototype of such an operator.

In an algebraic eigenvalue problem of the type (1.24) usually two steps are involved. In order to determine the eigenvectors $b_{i,l\sigma}$ the Hamilton matrix has to be evaluated first. Once the $b_{i,l\sigma}$ are known, other quantities, like the energy of the system can be calculated in a second step.[1] In the case of a multiplicative potential v M^2 integrals

$$\langle \eta_k | \hat{v} | \eta_l \rangle = \int d^3r \, \eta_k^*(\boldsymbol{r}) \, v(\boldsymbol{r}) \, \eta_l(\boldsymbol{r}) \qquad k,l = 1,\ldots M\,, \tag{C.1}$$

have to be evaluated in the first step.[2] Three aspects are relevant in this context:

- If v is a given potential the M^2 integrals have to be evaluated only once. However, the single-particle potential is often determined during the calculation, rather than given *a priori*. This is the case, in particular, for the HF scheme, which represents the starting point for many of the more advanced approaches. In a selfconsistent scheme the evaluation of the matrix elements $\langle \eta_k | \hat{v} | \eta_l \rangle$ has to be repeated a number of times. This repetition introduces an additional factor into the total computational cost, which, however, is independent of M and will be ignored in the following.
- On the other hand, the construction of v itself usually depends on M. The associated scaling cannot be determined without specification of a particular method and will therefore be examined later.

[1] In practice, these two steps often go hand in hand, of course.

[2] For Hermitian operators the actual number is $M(M+1)/2$, which for large M corresponds to $\mathcal{O}(M^2)$.

- It remains to address the cost of handling the spatial integral in (C.1). If the integral is known analytically, one can simply store the M^2 coefficients $\langle\eta_k|\hat{v}|\eta_l\rangle$ for repeated use. However, this is rarely the case, so that a numerical evaluation of (C.1) is usually unavoidable.[3] The summation over a spatial grid introduces an additional scaling factor of M, as the number of grid points required to represent M linearly independent basis functions is proportional to M. In the following the number of grid points will therefore simply be identified with M. As a result M^3 operations are needed in order to set up the table of all $\langle\eta_k|\hat{v}|\eta_l\rangle$, if numerical integration is used in Eq. (C.1).

Once the matrix elements $\langle\eta_k|\hat{v}|\eta_l\rangle$ are available and the eigenvalue problem (1.24) is solved, the evaluation of the associated energy,

$$\sum_{i=1}^{N}\langle\phi_i|\hat{v}|\phi_i\rangle = \sum_{i=1}^{N}\sum_{k,l}^{M}\sum_{\sigma} b^*_{i,k\sigma}b_{i,l\sigma}\langle\eta_k|\hat{v}|\eta_l\rangle\,, \tag{C.2}$$

involves a summation over N terms for each of the M^2 matrix elements kl (the multiplicities associated with spin are irrelevant at this point). The scaling of N and M is, however, intrinsically related, i.e. M increases linearly with N. For the present discussion N can therefore simply be replaced by M, so that one ends up with a total scaling of M^3.

It is instructive to compare this procedure with an alternative possibility for the calculation of (C.2). The first step of this second path is the evaluation of all orbitals (1.23), for which a summation over M terms is required for all $N = M$ orbitals on all M grid points. Once all $\phi_i(\boldsymbol{r})$ are stored, it takes M^2 operations to calculate the density

$$n(\boldsymbol{r}) = \sum_{\sigma}\sum_{i=1}^{N}|\phi_i(\boldsymbol{r}\sigma)|^2\,. \tag{C.3}$$

The energy (C.2) can finally be evaluated by numerical integration over $n(\boldsymbol{r})v(\boldsymbol{r})$, which is linear in M. Again one ends up with an M^3 scaling. In the alternative approach the storage of the $M \times M$ array $\phi_i(\boldsymbol{r})$ replaces the storage of the $M \times M$ array $\langle\eta_k|\hat{v}|\eta_l\rangle$ necessary in the first approach, so that no additional memory is needed.

The second approach can easily be extended to nonlocal single-particle potentials. In this case one would pre-evaluate the 1-particle density matrix

$$\gamma(\boldsymbol{r}\sigma,\boldsymbol{r}'\sigma') = \sum_{i=1}^{N}\phi_i(\boldsymbol{r}\sigma)\,\phi_i^*(\boldsymbol{r}'\sigma')\,, \tag{C.4}$$

rather than the density. This step scales as M^3. The integration

[3] The numerical integration can be avoided if v is expanded in terms of a separate basis set which allows an analytical treatment of $\langle\eta_k|\hat{v}|\eta_l\rangle$. This point will, however, not be expanded here.

$$\sum_{\sigma,\sigma'} \int d^3r \int d^3r' \; \gamma(\boldsymbol{r}\sigma,\boldsymbol{r}'\sigma') v(\boldsymbol{r}\sigma,\boldsymbol{r}'\sigma')$$

then requires M^2 operations.

The same arguments can be applied to the kinetic energy. This is immediately clear if the gradients of η_k can be evaluated analytically. However, even if the partial derivatives of η_k (or ϕ_i) have to be calculated numerically, the total scaling is not affected, as differentiation is linear in M.

In summary: the numerical calculation of the Hamilton matrix scales like M^3 with the basis set size, as long as the Hamiltonian consists only of single-particle operators, whose evaluation does not introduce an additional M-dependence. The same scaling behavior is found for the actual diagonalization of the Hamilton matrix by standard techniques.[4] In practice, however, the diagonalization is less time consuming than the evaluation of the matrix elements.

The situation becomes more complicated as soon as the Coulomb interaction, a 2-particle operator, is taken into account, i.e. as soon as the determination of $\hat{v}_{\mathrm{eff},\sigma\sigma'}$ is addressed. Let us explicitly consider the HF approximation in which only very specific Coulomb matrix elements are required. In order to extract the scaling behavior it is sufficient to analyze the exchange contribution

$$E_{\mathrm{x}} = -\frac{e^2}{2} \sum_{i,j=1}^{N} \sum_{\sigma,\sigma'} \int d^3r \int d^3r' \, \frac{\phi_i^*(\boldsymbol{r}\sigma)\phi_j^*(\boldsymbol{r}'\sigma')\phi_j(\boldsymbol{r}\sigma)\phi_i(\boldsymbol{r}'\sigma')}{|\boldsymbol{r}-\boldsymbol{r}'|} \,, \qquad \text{(C.5)}$$

which is the most demanding term in the HF approach. One possible method for the evaluation of (C.5) consists of the following sequence of operations:

1. evaluate and store $\phi_i(\boldsymbol{r}\sigma)$ (scales as M^3)
2. evaluate and store $\gamma(\boldsymbol{r}\sigma,\boldsymbol{r}'\sigma')$ (scales as M^3)
3. evaluate $E_{\mathrm{x}} = -\frac{e^2}{2} \sum_{\sigma,\sigma'} \int d^3r \int d^3r' \, \frac{|\gamma(\boldsymbol{r}\sigma,\boldsymbol{r}'\sigma')|^2}{|\boldsymbol{r}-\boldsymbol{r}'|}$ (scales as M^2)

A net scaling of M^3 is found. The same is true for the exchange contribution to the effective single-particle Hamiltonian

$$\begin{aligned} \sum_{j=1}^{N} (\eta_k \phi_j | \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} | \phi_j \eta_n) &= \sum_{j=1}^{N} \int d^3r \int d^3r' \, \frac{\eta_k^*(\boldsymbol{r})\phi_j^*(\boldsymbol{r}'\sigma')\phi_j(\boldsymbol{r}\sigma)\eta_n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} \qquad \text{(C.6)} \\ &= \int d^3r \eta_k^*(\boldsymbol{r}) \left[\int d^3r' \, \frac{\gamma(\boldsymbol{r}\sigma,\boldsymbol{r}'\sigma')}{|\boldsymbol{r}-\boldsymbol{r}'|} \eta_n(\boldsymbol{r}') \right] . \end{aligned}$$

The calculation of the quantity in brackets scales as M^3. Once it is stored for all $\boldsymbol{r}$ and n, one can perform the $\boldsymbol{r}$-integration for all k,l, which again scales as M^3.

However, the numerical evaluation of matrix elements of the Coulomb interaction is complicated by the singularity at $\boldsymbol{r} = \boldsymbol{r}'$ and by the long range of the inter-

[4] Here we ignore advanced techniques as iterative diagonalization [729], the Car-Parrinello method [730] and conjugate gradient methods [731, 732, 669] for brevity.

action. In addition, the procedure described, requires substantial memory as both the $M \times M$ arrays $\gamma(\boldsymbol{r}\sigma, \boldsymbol{r}'\sigma')$ and $\int d^3r' \gamma(\boldsymbol{r}\sigma, \boldsymbol{r}'\sigma')\eta_n(\boldsymbol{r}')/|\boldsymbol{r}-\boldsymbol{r}'|$ have to be stored simultaneously. It is therefore preferable to use basis functions for which the matrix elements

$$(\eta_k\eta_l||\eta_m\eta_n) = \int d^3r \int d^3r' \, \frac{\eta_k^*(\boldsymbol{r})\eta_l^*(\boldsymbol{r}')\eta_m(\boldsymbol{r})\eta_n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} \tag{C.7}$$

can be calculated analytically (like Gaussian or plane-wave basis functions). If the quantities $(\eta_k\eta_l||\eta_m\eta_n)$ are easily recalculated, it is not even necessary to store the matrix elements. Alternatively, one can store all $(\eta_k\eta_l||\eta_m\eta_n)$ before any other operation is performed. In this case the exchange term in the Hamilton matrix has the form

$$\sum_{j=1}^{N} (\eta_k\phi_j|\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}|\phi_j\eta_n) = \sum_{l,m=1}^{M}\sum_{j=1}^{N} b_{j,l\sigma'}^* b_{j,m\sigma}(\eta_k\eta_l||\eta_m\eta_n) \, , \tag{C.8}$$

which suggests an effort proportional to NM^4. However, the evaluation of the expression (C.8) and that of the exchange energy can again be split into several independent steps, which improves the scaling behavior. One first sums up the M^2 coefficients $\sum_{j=1}^{N} b_{j,l\sigma'}^* b_{j,m\sigma}$ and stores them. This step requires M^3 operations. In the second step the resulting matrix in l,m is folded with the known matrix elements $(\eta_k\eta_l||\eta_m\eta_n)$ for each pair k,n, which requires M^4 operations. If one again stores the resulting M^2 matrix elements, the summations over i,k,n required for the calculation of the complete exchange energy are independent of the previous steps, so that the third set of summations scales as M^2 (as $\sum_{i=1}^{N} b_{i,k\sigma}^* b_{i,n\sigma'}$ is already available). Taking all steps together, one ends up with a scaling of the HF scheme proportional to M^4 in this standard implementation.

As soon as arbitrary 2-particle matrix elements

$$(\phi_i\phi_j|\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}|\phi_k\phi_l)$$

have to be calculated, as is the case for all correlated *ab-initio* methods, the M^4-scaling can no longer be preserved by some clever sequence of operations. In addition, the scaling behavior again depends sensitively on the technical implementation. It is beyond the scope of this text to provide any details.

Appendix D
Explicit Density Functionals for the Kinetic Energy: Thomas-Fermi Models and Beyond

The theorem of Hohenberg and Kohn provides a justification of early density functional models which relied on a representation of the complete ground state energy E_0 in terms of the density,

$$E_0 = E[n_0] \,. \tag{D.1}$$

The first density functional of this type was the model of Thomas and Fermi (TF), which was established in the years 1927/28 [13, 14]. These authors considered a uniform gas of noninteracting electrons, the homogeneous electron gas (HEG) of Sect. 4.3, in order to derive a representation of the kinetic energy in terms of the density.

Their result can be derived by the Green's function techniques utilized in Sect. 4.3 for the discussion of the xc-energy of the HEG. In order to provide some alternative to this approach, however, a more elementary route for the derivation of the TF functional is taken in this Appendix. The Schrödinger equation for the single-particle states of the noninteracting electron gas reads

$$-\frac{\hbar^2 \boldsymbol{\nabla}^2}{2m} \phi_i(\boldsymbol{r}\sigma) = \varepsilon_i \phi_i(\boldsymbol{r}\sigma) \,. \tag{D.2}$$

The solutions of (D.2) are given by

$$\phi_{\boldsymbol{k}s}(\boldsymbol{r}\sigma) = C\, e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\, \chi_s(\sigma) \qquad \text{(quantum number } i \equiv \boldsymbol{k}s) \,, \tag{D.3}$$

with the Pauli spinors $\chi_s(\sigma)$ and the eigenvalues

$$\varepsilon_{\boldsymbol{k}} = \frac{\hbar^2 \boldsymbol{k}^2}{2m} \,. \tag{D.4}$$

Normalizable solutions can only be obtained if $\boldsymbol{k}$ is real. However, even in the case of real $\boldsymbol{k}$ the norm of $\phi_{\boldsymbol{k}s}$ is infinite, as soon as the complete space is considered. Moreover, the differential equation (D.2) allows arbitrary real values of $\boldsymbol{k}$, so that

one finds more than countably many states. It is thus necessary to regularize the problem by an additional boundary condition which ensures the normalizability of the $\phi_{\boldsymbol{k}s}$ and at the same time discretizes the spectrum. For this regularization one chooses a cubic box with sides of length L. Requiring periodic boundary conditions for all three Cartesian directions,

$$\phi_{\boldsymbol{k}s}(x+L,y,z,\sigma)=\phi_{\boldsymbol{k}s}(x,y+L,z,\sigma)=\phi_{\boldsymbol{k}s}(x,y,z+L,\sigma)=\phi_{\boldsymbol{k}s}(x,y,z,\sigma)\;, \quad \text{(D.5)}$$

leads to a quantization (i.e. discretization) of all components of $\boldsymbol{k}$,

$$k_i=\frac{2\pi}{L}\,\alpha_i \quad \text{with} \quad \alpha_i=0,\pm1,\pm2,\ldots \qquad (i=1,2,3)\;. \quad \text{(D.6)}$$

Normalization to 1 inside the box is obtained for $C=1/\sqrt{L^3}$,

$$\int_0^L dx\int_0^L dy\int_0^L dx\, e^{\frac{2\pi i}{L}(\boldsymbol{\alpha}'-\boldsymbol{\alpha})\cdot\boldsymbol{r}}\sum_{\sigma=\uparrow,\downarrow}\chi_s(\sigma)\chi_{s'}(\sigma)=L^3\,\delta_{\boldsymbol{\alpha}\boldsymbol{\alpha}'}\,\delta_{ss'}\;. \quad \text{(D.7)}$$

The single-particle states which are properly normalized within a cubic box are thus given by

$$\phi_{\boldsymbol{k}s}(\boldsymbol{r}\sigma)\;=\;\frac{e^{i\boldsymbol{k}\cdot\boldsymbol{r}}}{L^{3/2}}\,\chi_s(\sigma) \qquad \boldsymbol{k}=\frac{2\pi}{L}\,\boldsymbol{\alpha} \quad \text{with} \quad \alpha_i=0,\pm1,\pm2,\ldots\;. \quad \text{(D.8)}$$

In the ground state of the noninteracting homogeneous electron gas each level is filled with one spin-up and one spin-down electron. The number of levels which are occupied is determined by the number of particles in the box. The eigenvalue of the energetically highest occupied state is identified with the Fermi energy ε_{F}. Consequently, the density of the system is

$$\begin{aligned} n_0 &= \sum_{i=1}^{\infty}\Theta(\varepsilon_{\mathrm{F}}-\varepsilon_i)\sum_{\sigma=\uparrow,\downarrow}\phi_i^*(\boldsymbol{r}\sigma)\phi_i(\boldsymbol{r}\sigma) \\ &= \sum_{\alpha_1,\alpha_2,\alpha_3=0}^{\infty}\Theta(\varepsilon_{\mathrm{F}}-\varepsilon_{\boldsymbol{k}})\sum_{\sigma=\uparrow,\downarrow}\phi_{\boldsymbol{k}s}^*(\boldsymbol{r}\sigma)\phi_{\boldsymbol{k}s}(\boldsymbol{r}\sigma) \\ &= \sum_{\alpha_1,\alpha_2,\alpha_3=0}^{\infty}\Theta\left(\varepsilon_{\mathrm{F}}-\frac{\hbar^2\boldsymbol{k}^2}{2m}\right)\frac{2}{L^3}\;. \end{aligned} \quad \text{(D.9)}$$

Similarly one obtains for the kinetic energy per volume element

$$\begin{aligned} \frac{T_{\mathrm{s}}(V)}{V} &= \frac{1}{V}\sum_{i=1}^{\infty}\Theta(\varepsilon_{\mathrm{F}}-\varepsilon_i)\sum_{\sigma=\uparrow,\downarrow}\int_V d^3r\,\phi_i^*(\boldsymbol{r}\sigma)\frac{-\hbar^2\boldsymbol{\nabla}^2}{2m}\phi_i(\boldsymbol{r}\sigma) \\ &= \frac{1}{L^3}\sum_{\alpha_1,\alpha_2,\alpha_3=0}^{\infty}\Theta(\varepsilon_{\mathrm{F}}-\varepsilon_{\boldsymbol{k}})\sum_{\sigma=\uparrow,\downarrow}\int_0^L dx\int_0^L dy\int_0^L dz\,\phi_{\boldsymbol{k}s}^*(\boldsymbol{r}\sigma)\frac{\hbar^2\boldsymbol{k}^2}{2m}\phi_{\boldsymbol{k}s}(\boldsymbol{r}\sigma) \end{aligned}$$

$$= \sum_{\alpha_1,\alpha_2,\alpha_3=0}^{\infty} \Theta\left(\varepsilon_\mathrm{F} - \frac{\hbar^2\boldsymbol{k}^2}{2m}\right) \frac{2}{L^3}\frac{\hbar^2\boldsymbol{k}^2}{2m} \,. \tag{D.10}$$

At this point all expressions have been evaluated to a point at which the limit $L \to \infty$ can be taken, which leads back to the electron gas of infinite extension. In this limit the spacing between adjacent momenta $\boldsymbol{k}$ becomes infinitesimally small, so that the summation over all discrete values of $\boldsymbol{k}$ goes over into an integration over $\boldsymbol{k}$. The volume element of this $\boldsymbol{k}$-integration is obtained from the volume in $\boldsymbol{k}$-space which is associated with each of the discrete $\boldsymbol{k}$-values. For each of the Cartesian directions two neighboring k_i-values differ by $2\pi/L$, so that the $\boldsymbol{k}$-space volume per discrete $\boldsymbol{k}$-value is $(2\pi/L)^3$,

$$\begin{aligned} \Delta k_i = \frac{2\pi}{L}\Delta\alpha_i \quad &\Longrightarrow \quad \Delta\alpha_1\Delta\alpha_2\Delta\alpha_3 = \left(\frac{L}{2\pi}\right)^3 \Delta^3 k \\ \sum_{\alpha_1,\alpha_2,\alpha_3=0}^{\infty} \quad &\overset{L\to\infty}{\longrightarrow} \quad \left(\frac{L}{2\pi}\right)^3 \int d^3k \,. \end{aligned} \tag{D.11}$$

Introducing the Fermi momentum

$$k_\mathrm{F} := \frac{\sqrt{2m\varepsilon_\mathrm{F}}}{\hbar} \,, \tag{D.12}$$

the density and kinetic energy density are now easily evaluated using spherical coordinates,

$$\begin{aligned} n_0 &= \left(\frac{L}{2\pi}\right)^3 \int d^3k\, \Theta\left(k_\mathrm{F} - |\boldsymbol{k}|\right) \frac{2}{L^3} \\ &= \frac{k_\mathrm{F}^3}{3\pi^2} \end{aligned} \tag{D.13}$$

$$\begin{aligned} \frac{T_\mathrm{s}(V)}{V} &= \left(\frac{L}{2\pi}\right)^3 \int d^3k\, \Theta\left(k_\mathrm{F} - |\boldsymbol{k}|\right) \frac{2}{L^3}\frac{\hbar^2\boldsymbol{k}^2}{2m} \\ &= \frac{\hbar^2 k_\mathrm{F}^5}{10\pi^2 m} \,. \end{aligned} \tag{D.14}$$

Finally, one can invert the relation between n_0 and k_F,

$$k_\mathrm{F} = \left(3\pi^2 n_0\right)^{1/3} \,, \tag{D.15}$$

to end up with the desired relation between the kinetic energy density t_s and the density n_0,

$$t_\mathrm{s} \equiv \frac{T_\mathrm{s}(V)}{V} = \frac{\hbar^2(3\pi^2 n_0)^{5/3}}{10\pi^2 m} \,. \tag{D.16}$$

In order to apply this result to atoms, Thomas and Fermi (TF) relied on the local density approximation discussed in Sect. 4.3. In this approximation the energy density $t_s(\boldsymbol{r})$ of the actual inhomogeneous system is replaced by the energy density of the electron gas, Eq. (D.16), evaluated with the local density $n(\boldsymbol{r})$. The complete kinetic energy is then given by

$$T_s^{\mathrm{TF}} = \frac{3(3\pi^2)^{2/3}\hbar^2}{10m} \int d^3r\, n(\boldsymbol{r})^{5/3} \,. \tag{D.17}$$

This expression is manifestly a density functional. As it is derived from the non-interacting gas it represents an approximation for the Kohn-Sham kinetic energy functional $T_s[n]$, introduced in Sect. 3.1.

The total energy functional of Thomas and Fermi neglected all exchange and correlation effects, so that only the direct Coulomb repulsion (Hartree energy) and the coupling to the external potential remain,

$$E^{\mathrm{TF}}[n] \;=\; T_s^{\mathrm{TF}}[n] + \frac{e^2}{2}\int d^3r \int d^3r'\, \frac{n(\boldsymbol{r})\, n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \int d^3r\, v_{\mathrm{ext}}(\boldsymbol{r}) n(\boldsymbol{r}) \,. \tag{D.18}$$

Applications can be based directly on the variational equation (2.38), reflecting the minimum principle (2.28). The welcome feature is the fact that the variational approach reduces the many-particle problem to a form which is independent of the particle number.

Considerable effort was expended in order to improve this model. The first and most important step was the inclusion of exchange by Dirac in 1930 [131]. Dirac followed the path of Thomas and Fermi and considered the exchange energy of the uniform electron gas. The exact exchange energy of the gas in the cubic box of volume $V = L^3$ has the form

$$\begin{aligned} E_x(V) = -\frac{e^2}{2} \sum_{i,j=1}^{\infty} \Theta(\varepsilon_F - \varepsilon_i)\Theta(\varepsilon_F - \varepsilon_j) \\ \times \sum_{\sigma,\sigma'=\uparrow,\downarrow} \int_V d^3r \int d^3r'\, \frac{\phi_i^*(\boldsymbol{r}\sigma)\phi_j(\boldsymbol{r}\sigma)\phi_j^*(\boldsymbol{r}'\sigma')\phi_i(\boldsymbol{r}'\sigma')}{|\boldsymbol{r}-\boldsymbol{r}'|} \,. \end{aligned} \tag{D.19}$$

Insertion of the states (D.8) of the uniform gas yields for the exchange energy per volume element (after an appropriate shift of $\boldsymbol{r}'$ by $\boldsymbol{r}$)

$$e_x \equiv \frac{E_x(V)}{V} = -e^2 \sum_{\boldsymbol{\alpha}\boldsymbol{\beta}} \Theta\left(k_F - |\boldsymbol{k}_{\boldsymbol{\alpha}}|\right) \Theta\left(k_F - |\boldsymbol{k}_{\boldsymbol{\beta}}|\right) \int d^3r'\, \frac{e^{i(\boldsymbol{k}_{\boldsymbol{\alpha}} - \boldsymbol{k}_{\boldsymbol{\beta}})\cdot\boldsymbol{r}'}}{L^6 |\boldsymbol{r}'|} \,. \tag{D.20}$$

One can now use the fact that for $L \to \infty$ the summation over all integers $\boldsymbol{\alpha}$ can be replaced by an integration over $\boldsymbol{k}$, Eq. (D.11), to obtain

$$e_x \;=\; -e^2 \int \frac{d^3k}{(2\pi)^3} \int \frac{d^3q}{(2\pi)^3}\, \Theta(k_F - |\boldsymbol{k}|)\Theta(k_F - |\boldsymbol{q}|) \int d^3r'\, \frac{e^{i(\boldsymbol{k}-\boldsymbol{q})\cdot\boldsymbol{r}'}}{|\boldsymbol{r}'|} \,. \tag{D.21}$$

Next, the $\boldsymbol{r}'$-integration can be carried out by introducing a suitable intermediate regularization factor $e^{-\mu|\boldsymbol{r}'|}$ in the integral and taking the limit $\mu \to 0$ after integration (compare Eq. (4.144) and the subsequent discussion in Sect. 4.4.1),

$$e_{\mathrm{x}} = -e^2 \int \frac{d^3k}{(2\pi)^3} \int \frac{d^3q}{(2\pi)^3} \Theta(k_{\mathrm{F}} - |\boldsymbol{k}|)\Theta(k_{\mathrm{F}} - |\boldsymbol{q}|) \frac{4\pi}{(\boldsymbol{k}-\boldsymbol{q})^2} \,. \tag{D.22}$$

One now first performs the $\boldsymbol{q}$-integration. Choosing the z-axis of the coordinate system for $\boldsymbol{q}$ so that it is parallel to $\boldsymbol{k}$, the $\boldsymbol{q}$-integration can be done in spherical coordinates,

$$\begin{aligned} e_{\mathrm{x}} &= -\frac{e^2}{\pi} \int \frac{d^3k}{(2\pi)^3} \Theta(k_{\mathrm{F}} - k) \int_0^{k_{\mathrm{F}}} q^2 dq \int_{-1}^{+1} d\cos(\theta) \, \frac{1}{k^2 + q^2 - 2kq\cos(\theta)} \\ &= \frac{e^2}{2\pi^3} \int_0^{k_{\mathrm{F}}} k dk \int_0^{k_{\mathrm{F}}} q dq \, \left[\ln|k-q| - \ln(k+q)\right] . \end{aligned}$$

The remaining integrations are straightforward, after splitting the range of the inner integration over q into the subregimes $[0,k]$ and $[k,k_{\mathrm{F}}]$,

$$e_{\mathrm{x}} = -\frac{e^2}{4\pi^3} k_{\mathrm{F}}^4 . \tag{D.23}$$

Insertion of the Fermi momentum (D.15) then leads to

$$e_{\mathrm{x}} = -\frac{e^2}{4\pi^3} \left(3\pi^2 n_0\right)^{4/3} \,. \tag{D.24}$$

Using the local density approximation, one finally arrives at the density functional

$$E_{\mathrm{x}}^{\mathrm{D}}[n] = -\frac{3(3\pi^2)^{1/3} e^2}{4\pi} \int d^3r \, n(\boldsymbol{r})^{4/3} \,. \tag{D.25}$$

$E_{\mathrm{x}}^{\mathrm{D}}[n]$ is an approximation for the exact exchange energy functional $E_{\mathrm{x}}[n]$ of DFT. As is clear from its construction, $E_{\mathrm{x}}^{\mathrm{D}}[n]$ is nothing but the LDA for exchange, Eqs. (4.99), (4.109), in modern terminology. Adding this term to the energy (D.18) constitutes the Thomas-Fermi-Dirac model.

The next step towards extending the TF model was taken by von Weizsäcker in 1935 [174]. Von Weizsäcker observed that one can express the kinetic energy of a single particle in terms of the density. In fact, if there is only one particle bound by some potential, the corresponding ground state orbital

$$\phi_i(\boldsymbol{r}\sigma) \;=\; \varphi_0(\boldsymbol{r})\, \chi_s(\sigma)$$

may be chosen real, so that its kinetic energy may be written as[1]

[1] The surface term does not contribute in the partial integration since a normalizable orbital decays sufficiently rapidly for $|\boldsymbol{r}| \to \infty$.

$$T_{\rm s} \;=\; \sum_{\sigma=\uparrow,\downarrow} \int d^3r\, \phi_i^*(\boldsymbol{r}\sigma) \frac{-\hbar^2\boldsymbol{\nabla}^2}{2m} \phi_i(\boldsymbol{r}\sigma) \;=\; \int d^3r\, \frac{[\hbar\boldsymbol{\nabla}\varphi_0(\boldsymbol{r})]^2}{2m} \,. \qquad \text{(D.26)}$$

The corresponding density is given by

$$n(\boldsymbol{r}) \;=\; \sum_{\sigma=\uparrow,\downarrow} |\phi_i(\boldsymbol{r}\sigma)|^2 \;=\; \varphi_0(\boldsymbol{r})^2 \,.$$

Insertion into (D.26) leads to the von Weizsäcker functional

$$T_{\rm s}^{\rm vW}[n] = \frac{\hbar^2}{m} \int d^3r\, \frac{[\boldsymbol{\nabla} n(\boldsymbol{r})]^2}{8n(\boldsymbol{r})} \,. \qquad \text{(D.27)}$$

This density functional also represents the exact kinetic energy in the case of a noninteracting 2-particle system in which both particles occupy the same orbital φ_0, but have opposite spins. $T_{\rm s}^{\rm vW}[n]$ thus agrees with the exact $T_{\rm s}[n]$ of Kohn-Sham theory for a single particle and a spin-saturated pair of two particles.

The expression for $T_{\rm s}^{\rm vW}[n]$ also indicates how the TF kinetic energy can be extended in order to better account for the inhomogeneity of real systems: obviously, the gradient of the density is the simplest purely density-dependent measure of the inhomogeneity in a many-particle system. The only parameter-free expression for $t_{\rm s}$ which (i) depends only locally on $\boldsymbol{\nabla} n$ and (ii) does not depend on the characteristics of the external potential (as for instance on some preferred axis) is the functional (D.27). It is thus no surprise that a systematic derivation of gradient corrections for the kinetic energy, either using some form of the so-called commutator expansion [173] or following the lines of Sect. 4.4, leads to an expression which differs from $T_{\rm s}^{\rm vW}[n]$ only by an overall prefactor $\lambda = 1/9$ (for all details, including higher order gradient corrections [175, 733, 194, 195, 734], see Chap. 5 of [7]). Adding $\lambda T_{\rm s}^{\rm vW}[n]$ to $E^{\rm TF}[n] + E_{\rm x}^{\rm D}[n]$ constitutes the Thomas-Fermi-Dirac-Weizsäcker model.

Without going into detail, we list some further extensions of the TF-model:

- First correlation contributions were introduced by Wigner as early as 1934 [138] (see Sect. 4.3.4).
- Gradient corrections to the Dirac exchange energy were calculated subsequently, but were found to lead to a divergent behavior for small and large separations from the nucleus in atoms—compare Sect. 4.4.3.

Nonetheless, the endeavors to improve TF-type density functionals were essentially abandoned until recently, since the explicitly density-dependent representation of $T_{\rm s}$ used in these models does not allow to reproduce shell structure.

Renewed interest in functionals of the type (D.1) has been stimulated by the N^3-scaling of the Kohn-Sham approach with system size: if one wants to perform calculations for truly large quantum systems without any periodicity or other symmetry (e.g. disordered solids or huge (bio)molecules), an N^3-scaling is still prohibitive. In this case use of a *kinetic energy density functional* (KEDF) is highly attractive. In view of the limitations of the TF-type semi-local functionals a fully nonlocal ansatz is chosen for modern KEDFs [735–749]. The general form of these approximations

is[2]

$$T_{\rm s}^{\rm nl}[n] = T_{\rm s}^{\rm TF}[n] + T_{\rm s}^{\rm vW}[n] + \frac{\hbar^2 3(3\pi^2)^{2/3}}{10m} \int d^3r\, d^3r'\, n(\boldsymbol{r})^{\alpha} w_{\alpha\beta}\left(\xi_\gamma(\boldsymbol{r},\boldsymbol{r}'), \boldsymbol{r}-\boldsymbol{r}'\right) n(\boldsymbol{r}')^{\beta}\,, \quad \text{(D.28)}$$

with the *2-body Fermi wavevector*

$$\xi_\gamma(\boldsymbol{r},\boldsymbol{r}') = \left[\frac{(3\pi^2 n(\boldsymbol{r}))^{\gamma/3} + (3\pi^2 n(\boldsymbol{r}'))^{\gamma/3}}{2}\right]^{1/\gamma} \quad \text{(D.29)}$$

(the structure of (D.28) can be motivated by scaling arguments [750]). By construction the functional $T_{\rm s}^{\rm nl}[n]$ can be exact for the electron gas with $\boldsymbol{\nabla} n = \boldsymbol{0}$ and for a 2-particle system, if the density-dependent kernel w is chosen appropriately. So, obviously one has the requirement

$$w_{\alpha\beta}\left(\xi_\gamma, \boldsymbol{r}-\boldsymbol{r}'\right) \;=\; 0$$

in the electron gas limit. Moreover, in order to recover the exact linear response result for the weakly inhomogeneous electron gas, Eq. (4.156), the kernel has to satisfy a differential equation, which allows to determine its shape. In fact, this differential equation can even be solved analytically [749], which, in spite of the nonlocality of $\xi_\gamma(\boldsymbol{r},\boldsymbol{r}')$, leads to an $N\ln(N)$ scaling of the computational effort with the system size. KEDFs can therefore provide the basis for multiscale modelling.

Selfconsistent calculations with KEDFs are usually based on pseudopotentials. The pseudopotentials have to be local, as projecting out part of the all-electron Hilbert space is not possible, if no states are involved. However, an accurate description by local pseudopotentials can only be expected for simple metals. Applications of KEDFs to bulk aluminum, aluminum surfaces and aluminum clusters [742, 743, 746, 749] demonstrated that the functional (D.28) accurately reproduces the geometry, energetics (including vacancy formation) and density profiles of the full Kohn-Sham solutions. In particular, one finds very accurate results for the relative energies of different crystal structures [746]. KEDFs perform even better for sodium [742, 743].

[2] Sometimes, even several nonlocal kernels of the form (D.28) are superposed [745],

$$\sum_{\alpha\beta} \lambda_{\alpha\beta} \left\langle n(\boldsymbol{r})^{\alpha}\, w_{\alpha\beta}\, n(\boldsymbol{r}')^{\beta} \right\rangle ,$$

in order to allow for more flexibility. In this case $\sum_{\alpha\beta} \lambda_{\alpha\beta} = 1$ is required.

Appendix E
Asymptotic Behavior of Quasi-Particle Amplitudes

In this Appendix the asymptotic behavior of the quasi-particle amplitudes f_k, Eq. (3.104), for the case of finite systems is extracted from the differential equation (3.112). One starts by noting that a multipole expansion of the interaction $w(\boldsymbol{r},\boldsymbol{r}')$ is legitimate for large $|\boldsymbol{r}|$, as $\langle\Psi_k^{N-1}|\hat{n}(\boldsymbol{r}')|\Psi_l^{N-1}\rangle$ decays exponentially for large $|\boldsymbol{r}'|$—only bound states k are of interest, so that $|\Psi_k^{N-1}\rangle$ represents a localized wavefunction which vanishes exponentially for large $|\boldsymbol{r}|$. Restricting the discussion to the Coulomb interaction, one has

$$w(\boldsymbol{r},\boldsymbol{r}') = \frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|} = \frac{e^2}{|\boldsymbol{r}|}\left\{1+\frac{\boldsymbol{r}\cdot\boldsymbol{r}'}{|\boldsymbol{r}|^2}+\ldots\right\}. \tag{E.1}$$

Insertion into the nonlocal term in Eq. (3.112) leads to

$$\begin{aligned}&\sum_l \int d^3r'\, w(\boldsymbol{r},\boldsymbol{r}')\,\langle\Psi_k^{N-1}|\hat{n}(\boldsymbol{r}')|\Psi_l^{N-1}\rangle\, f_l(\boldsymbol{r}\sigma)\\ &= \frac{e^2}{|\boldsymbol{r}|}\sum_l\left\{(N-1)\delta_{kl}+\frac{\boldsymbol{r}}{|\boldsymbol{r}|^2}\cdot\langle\Psi_k^{N-1}|\int d^3r'\,\boldsymbol{r}'\hat{n}(\boldsymbol{r}')|\Psi_l^{N-1}\rangle\right\} f_l(\boldsymbol{r}\sigma)\\ &\quad+\mathcal{O}(|\boldsymbol{r}|^{-3}).\end{aligned} \tag{E.2}$$

The kernel of the first order term is exactly the operator of the dipole moment,

$$\hat{\boldsymbol{D}} = e^2\int d^3r\,\boldsymbol{r}\,\hat{n}(\boldsymbol{r}). \tag{E.3}$$

A multipole expansion is also possible for the external potential. Using again the Coulomb form, one obtains

$$v_{\rm ext}(\boldsymbol{r}) = -\sum_\alpha \frac{Z_\alpha e^2}{|\boldsymbol{r}-\boldsymbol{R}_\alpha|} = -\frac{Ze^2}{|\boldsymbol{r}|}-\frac{\boldsymbol{r}}{|\boldsymbol{r}|^3}\cdot\sum_\alpha Z_\alpha e^2\boldsymbol{R}_\alpha+\ldots \quad;\quad Z=\sum_\alpha Z_\alpha, \tag{E.4}$$

where Z_α and $\boldsymbol{R}_\alpha$ denote the charge and position of nucleus α. Insertion of (E.2)–(E.4) into (3.112) yields the asymptotic differential equation for the f_k,

$$\left\{-\frac{\hbar^2\boldsymbol{\nabla}^2}{2m}-\frac{(Z-N+1)e^2}{|\boldsymbol{r}|}-\hbar\omega_k\right\}f_k(\boldsymbol{r}\sigma)+\frac{\boldsymbol{r}}{|\boldsymbol{r}|^3}\cdot\sum_l \boldsymbol{D}_{kl}\,f_l(\boldsymbol{r}\sigma)=0\,. \tag{E.5}$$

All electronic and nuclear dipole contributions have been absorbed into $\boldsymbol{D}_{kl}$. The asymptotically leading term of the potential in (E.5) is the spherically symmetric monopole term. The general solution of (E.5) thus has the form

$$f_k(\boldsymbol{r}\sigma)\;\underset{|\boldsymbol{r}|\to\infty}{\longrightarrow}\;\left[\sum_{lm}c_{k\sigma}^{lm}\,Y_{lm}(\Omega)\right]r^{\beta_{k\sigma}-1}\,e^{-\alpha_{k\sigma}r}\,, \tag{E.6}$$

with coefficients $c_{k\sigma}^{lm}$, $\beta_{k\sigma}$ and $\alpha_{k\sigma}$ which remain to be determined. Insertion into (E.5) gives

$$\begin{aligned}0=\sum_{lm}Y_{lm}(\Omega)\Bigg\{&\left[\frac{\partial^2}{\partial r^2}-\frac{l(l+1)}{r^2}+2\frac{m}{\hbar^2}\left(\hbar\omega_k+\frac{(Z-N+1)e^2}{r}\right)\right]c_{k\sigma}^{lm}\,r^{\beta_{k\sigma}}\\&-2\frac{m}{\hbar^2}\,\frac{\boldsymbol{r}}{r^3}\cdot\sum_n\boldsymbol{D}_{kn}\,c_{n\sigma}^{lm}\,r^{\beta_{n\sigma}}\,e^{(\alpha_{k\sigma}-\alpha_{n\sigma})r}\Bigg\}e^{-\alpha_{k\sigma}r}\,.\end{aligned} \tag{E.7}$$

As all f_k are coupled by the dipole moment matrix elements $\boldsymbol{D}_{kn}$ and these matrix elements do not vanish for $k\neq n$, all f_k must have the same exponential decay. This statement can be verified by reductio ad absurdum. Assume that there is one amplitude f_q which shows the weakest decay, i.e. $\alpha_{q\sigma}<\alpha_{k\sigma}$ for all $k\neq q$. Now consider the asymptotic equation for $k\neq q$. The dipole contribution of f_q dominates this asymptotic equation, i.e. the sum over n breaks down to the single term with $n=q$. Due to $\alpha_{k\sigma}-\alpha_{q\sigma}>0$, however, this term diverges exponentially, thus requiring $c_{q\sigma}^{lm}=0$. One ends up with a contradiction, so that all $\alpha_{k\sigma}$ must be identical. The same result is found for Hartree-Fock orbitals [751], which also satisfy coupled equations of the type (E.5).

With $\alpha_{k\sigma}\equiv\alpha_\sigma$ Eq. (E.7) reduces to

$$\begin{aligned}0=\sum_{lm}Y_{lm}(\Omega)\Bigg\{&\left[\frac{\beta_{k\sigma}(\beta_{k\sigma}-1)}{r^2}-2\frac{\alpha_\sigma\beta_{k\sigma}}{r}+\alpha_\sigma^2-\frac{l(l+1)}{r^2}\right.\\&\left.+2\frac{m}{\hbar^2}\left(\hbar\omega_k+\frac{(Z-N+1)e^2}{r}\right)\right]c_{k\sigma}^{lm}\,r^{\beta_{k\sigma}}\\&-2\frac{m}{\hbar^2}\,\frac{\boldsymbol{r}}{r^3}\cdot\sum_n\boldsymbol{D}_{kn}\,c_{n\sigma}^{lm}\,r^{\beta_{n\sigma}}\Bigg\}.\end{aligned} \tag{E.8}$$

Consider now the amplitude q with the largest exponent $\beta_{k\sigma}$,

$$\beta_{q\sigma}>\beta_{k\sigma}\quad\forall\,k\neq q\,. \tag{E.9}$$

In the asymptotic equation for f_q the dipole term is suppressed by $1/r$ with respect to the two leading orders. Consequently one obtains

$$\alpha_\sigma^2 = -2\frac{m}{\hbar}\omega_q\,; \qquad \beta_{q\sigma} = \sqrt{\frac{m}{\hbar^2}}\frac{(Z-N+1)e^2}{\sqrt{-2\hbar\omega_q}}\,. \tag{E.10}$$

The largest exponent is therefore found for the smallest $|\omega_q|$, i.e. for $q = 0$,

$$\alpha_\sigma = \sqrt{\frac{-2m\omega_0}{\hbar}} = \frac{\sqrt{2m\,\mathrm{IP}}}{\hbar}\,; \qquad \beta_{0\sigma} = \sqrt{\frac{m}{\hbar^2}}\frac{(Z-N+1)e^2}{\sqrt{-2\hbar\omega_0}}\,. \tag{E.11}$$

All other k must be suppressed relative to this leading amplitude by a factor of $1/r^2$, in order to satisfy the asymptotic equation. Only in this case can the leading contribution of the dipole term be compensated by the leading contribution of the remaining terms in the asymptotic equation (E.8) for all states $k \neq 0$,

$$0 = \sum_{lm} Y_{lm}(\Omega)\left\{2\hbar(\omega_k-\omega_0)c_{k\sigma}^{lm}\,r^{\beta_{k\sigma}} - 2\,\frac{\boldsymbol{r}}{r^3}\cdot\boldsymbol{D}_{k0}\,c_{0\sigma}^{lm}\,r^{\beta_{0\sigma}}\right\} \tag{E.12}$$

(as $\beta_{0\sigma} > \beta_{n\sigma}$ for $n > 0$, the sum over n breaks down to a single term). One ends up with

$$\beta_{k\sigma} = \beta_{0\sigma} + 2 \quad \forall\, k > 0 \tag{E.13}$$

and the coefficients $c_{k\sigma}^{lm}$ have to satisfy

$$0 = \sum_{lm} Y_{lm}(\Omega)\left\{\hbar(\omega_k-\omega_0)c_{k\sigma}^{lm} - \frac{\boldsymbol{r}}{r}\cdot\boldsymbol{D}_{k0}\,c_{0\sigma}^{lm}\right\}. \tag{E.14}$$

Equations (E.6), (E.11), (E.13), (E.14) determine the asymptotic behavior of all f_k.

Appendix F
Quantization of Noninteracting Fermions in Relativistic Quantum Field Theory

This Appendix summarizes the quantum field theoretical description of noninteracting spin-1/2 particles. In particular, the quantization procedure is reviewed, emphasizing the close relation between the minimum principle for the ground state energy and the renormalization scheme. At the same time this Appendix provides the background for the field theoretical treatment of the KS system, i.e. Eqs. (8.76)–(8.89). For brevity, we use $\hbar = c = 1$ in this Appendix.

The starting point is the *classical* field theory characterized by the Lagrangian

$$\mathscr{L}_{\mathrm{s}}(x) = \mathscr{L}_{\mathrm{e}}(x) + \mathscr{L}_{\mathrm{ext}}(x) = \overline{\psi}_{\mathrm{s}}(x)\left[i\gamma^{\mu}\partial_{\mu} - m + e\gamma^{\mu}V_{\mu}(\boldsymbol{x})\right]\psi_{\mathrm{s}}(x)\,, \tag{F.1}$$

where $V^{\mu}(\boldsymbol{x})$ is a given, stationary external potential. V^{μ} may either represent some nuclear potential or a composite object as the total KS potential v_{s}^{μ}. The orthonormal eigenfunctions of the corresponding classical field equations will be denoted by ϕ_k, the associated single-particle energies by ε_k,

$$\left[-i\boldsymbol{\alpha}\cdot\boldsymbol{\nabla} + \beta m - e\alpha_{\mu}V^{\mu}(\boldsymbol{x})\right]\phi_k(\boldsymbol{x}) = \varepsilon_k\phi_k(\boldsymbol{x})\,. \tag{F.2}$$

A sketch of the eigenvalue spectrum resulting in the case of an attractive V^{μ} is shown in Fig. F.1. It consists of a continuum of negative energy states with energies below $-m$ (i.e. $-mc^2$), a continuum of positive energy states with energies above $+m$ and a countable number of discrete levels in between (which are at least twofold degenerate in the case of time-reversal invariant systems).

In the first step one has to quantize the classical field theory. The standard canonical quantization via equal-time commutation relations for the fermion field operator $\hat{\psi}_{\mathrm{s}}$ yields

$$\hat{\psi}_{\mathrm{s}}(x) = \sum_k \hat{b}_k\phi_k(\boldsymbol{x})e^{-i\varepsilon_k t}\,, \qquad \hat{\psi}_{\mathrm{s}}^{\dagger}(x) = \sum_k \hat{b}_k^{\dagger}\phi_k^{\dagger}(\boldsymbol{x})e^{i\varepsilon_k t}\,, \tag{F.3}$$

where the sums run over all negative and positive energy solutions of (F.2) and the operator-valued expansion coefficients $\hat{b}_k$ satisfy the commutation relations

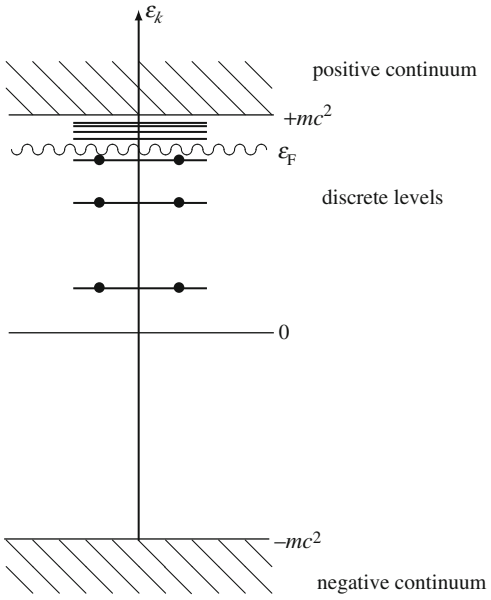


Fig. F.1 Eigenvalue spectrum of noninteracting fermions in attractive potential.

$$\left\{\hat{b}_k, \hat{b}_l\right\} = \left\{\hat{b}_k^\dagger, \hat{b}_l^\dagger\right\} = 0\,, \qquad \left\{\hat{b}_k, \hat{b}_l^\dagger\right\} = \delta_{kl}\,. \tag{F.4}$$

$\hat{b}_k$ destroys a particle in state k, so that $\hat{\psi}_\mathrm{s}(x)$ destroys a particle at point $\boldsymbol{x}$ and time t. The canonical Hamiltonian obtained from (F.1) by insertion of (F.3) is given by

$$\begin{aligned}\hat{H}_\mathrm{s} &= \int d^3x\; \hat{\psi}_\mathrm{s}^\dagger(x)\Big[-i\boldsymbol{\alpha}\cdot\boldsymbol{\nabla} + \beta m - e\alpha_\mu V^\mu(\boldsymbol{x})\Big]\hat{\psi}_\mathrm{s}(x) \\ &= \sum_k \varepsilon_k \hat{b}_k^\dagger \hat{b}_k \;=\; \sum_{\varepsilon_k \le -m} \varepsilon_k \hat{b}_k^\dagger \hat{b}_k + \sum_{-m<\varepsilon_k} \varepsilon_k \hat{b}_k^\dagger \hat{b}_k\,,\end{aligned} \tag{F.5}$$

while the canonical charge operator reads

$$\hat{Q}_\mathrm{s} = \int d^3x\; \hat{\psi}_\mathrm{s}^\dagger(x)\hat{\psi}_\mathrm{s}(x) = \sum_k \hat{b}_k^\dagger \hat{b}_k = \sum_{\varepsilon_k \le -m} \hat{b}_k^\dagger \hat{b}_k + \sum_{-m<\varepsilon_k} \hat{b}_k^\dagger \hat{b}_k\,. \tag{F.6}$$

A naive application of Fermi statistics would require that all levels below the Fermi energy ε_F are occupied for the ground state $|\Phi_\mathrm{s}\rangle$ of this system. This would imply that, in addition to a finite number of discrete levels between $-m$ and ε_F, all negative energy states are filled,

$$|\Phi_\mathrm{s}\rangle = \prod_{\varepsilon_k \le \varepsilon_\mathrm{F}} \hat{b}_k^\dagger |0_\mathrm{s}'\rangle\,, \tag{F.7}$$

where $|0'_{\rm s}\rangle$ denotes the vacuum with the property that $\hat{b}_k|0'_{\rm s}\rangle = 0$ for all k. Obviously, $\hat{H}_{\rm s}$ is not bounded from below for this kind of state and the charge $\langle\Phi_{\rm s}|\hat{Q}_{\rm s}|\Phi_{\rm s}\rangle$ diverges.

The well-established solution to this problem is the reinterpretation of the negative energy states as unoccupied antiparticle states with positive energy $-\varepsilon_k$. The annihilation of a particle with $\varepsilon_k \leq -m$ via $\hat{b}_k$ then has to be understood as the creation of an antiparticle and vice versa, which is reflected by a redefinition of the negative energy annihilation and creation operators,

$$\hat{d}_k := \hat{b}_k^\dagger\,, \qquad \hat{d}_k^\dagger := \hat{b}_k \qquad \forall k \text{ with } \varepsilon_k \leq -m\,. \tag{F.8}$$

Equations (F.3), (F.4) then take on the forms

$$\left\{\hat{b}_k, \hat{b}_l\right\} = \left\{\hat{b}_k^\dagger, \hat{b}_l^\dagger\right\} = \left\{\hat{d}_k, \hat{d}_l\right\} = \left\{\hat{d}_k^\dagger, \hat{d}_l^\dagger\right\} = \left\{\hat{d}_k^{(\dagger)}, \hat{b}_l^{(\dagger)}\right\} = 0 \tag{F.9}$$

$$\left\{\hat{b}_k, \hat{b}_l^\dagger\right\} = \left\{\hat{d}_k, \hat{d}_l^\dagger\right\} = \delta_{kl} \tag{F.10}$$

$$\hat{\psi}_{\rm s}(x) = \sum_{\varepsilon_k \leq -m} \hat{d}_k^\dagger \phi_k(\boldsymbol{x}) e^{-i\varepsilon_k t} + \sum_{-m < \varepsilon_k} \hat{b}_k \phi_k(\boldsymbol{x}) e^{-i\varepsilon_k t}\,, \tag{F.11}$$

so that $\hat{\psi}_{\rm s}(x)$ now annihilates a unit of charge at point $\boldsymbol{x}$ and time t, rather than a particle. The vacuum must be redefined accordingly,

$$\hat{b}_k|0_{\rm s}\rangle = 0 \quad \forall\, \varepsilon_k > -m\,, \qquad \hat{d}_k|0_{\rm s}\rangle = 0 \quad \forall\, \varepsilon_k \leq -m\,, \tag{F.12}$$

in order to ensure that neither a particle nor an antiparticle is present in the state $|0_{\rm s}\rangle$. The ground state of the N-particle system is then simply given by N particles added to this vacuum,

$$|\Phi_{\rm s}\rangle = \prod_{-m < \varepsilon_k \leq \varepsilon_{\rm F}} \hat{b}_k^\dagger |0_{\rm s}\rangle\,. \tag{F.13}$$

Insertion of (F.8) into the Hamiltonian yields

$$\begin{aligned} \hat{H}_{\rm s} &= \sum_{\varepsilon_k \leq -m} \varepsilon_k \hat{d}_k \hat{d}_k^\dagger + \sum_{-m < \varepsilon_k} \varepsilon_k \hat{b}_k^\dagger \hat{b}_k \\ &= \sum_{\varepsilon_k \leq -m} (-\varepsilon_k) \hat{d}_k^\dagger \hat{d}_k + \sum_{-m < \varepsilon_k} \varepsilon_k \hat{b}_k^\dagger \hat{b}_k + \sum_{\varepsilon_k \leq -m} \varepsilon_k\,, \end{aligned} \tag{F.14}$$

so that one finds as ground state and vacuum energies,

$$\langle\Phi_{\rm s}|\hat{H}_{\rm s}|\Phi_{\rm s}\rangle = \sum_{\varepsilon_k \leq \varepsilon_{\rm F}} \varepsilon_k\,, \qquad \langle 0_{\rm s}|\hat{H}_{\rm s}|0_{\rm s}\rangle = \sum_{\varepsilon_k \leq -m} \varepsilon_k\,. \tag{F.15}$$

Due to the simultaneous redefinition of the negative energy states and the vacuum, Eq. (F.12), the Hamiltonian is still not bounded from below. Its boundedness must be implemented by a renormalization of the energy scale, i.e. by explicit subtraction of the vacuum expectation value of $\hat{H}_{\rm s}$,

$$\hat{H}'_{\mathrm{s,R}} := \hat{H}_{\mathrm{s}} - \langle 0_{\mathrm{s}}|\hat{H}_{\mathrm{s}}|0_{\mathrm{s}}\rangle \qquad \Longrightarrow \qquad \langle \Phi_{\mathrm{s}}|\hat{H}'_{\mathrm{s,R}}|\Phi_{\mathrm{s}}\rangle = \sum_{-m<\varepsilon_k\le\varepsilon_{\mathrm{F}}} \varepsilon_k \,. \tag{F.16}$$

For this renormalized Hamiltonian one can then immediately establish a minimum principle, since any admixture of a single-particle state above ε_{F} to the N-particle state leads to a well-defined energy which is higher than $\langle \Phi_{\mathrm{s}}|\hat{H}'_{\mathrm{s,R}}|\Phi_{\mathrm{s}}\rangle$. Moreover, if one adds an antiparticle to $|\Phi_{\mathrm{s}}\rangle$, the resulting energy is at least m (i.e. mc^2) above the ground state energy (in the noninteracting theory a particle-antiparticle pair cannot annihilate). The same procedure is applied to $\hat{Q}_{\mathrm{s}}$,

$$\hat{Q}'_{\mathrm{s,R}} := \hat{Q}_{\mathrm{s}} - \langle 0_{\mathrm{s}}|\hat{Q}_{\mathrm{s}}|0_{\mathrm{s}}\rangle = -\sum_{\varepsilon_k\le -m} \hat{d}_k^\dagger \hat{d}_k + \sum_{-m<\varepsilon_k} \hat{b}_k^\dagger \hat{b}_k \tag{F.17}$$

$$\Longrightarrow \langle \Phi_{\mathrm{s}}|\hat{Q}'_{\mathrm{s,R}}|\Phi_{\mathrm{s}}\rangle = \sum_{-m<\varepsilon_k\le\varepsilon_{\mathrm{F}}} 1 \,, \tag{F.18}$$

which directly illustrates the opposite charges of particles and antiparticles. The subtraction of the vacuum expectation values in (F.16) and (F.17) is equivalent to a normal-ordering of the creation/annihilation operators in $\hat{H}_{\mathrm{s}}$ and $\hat{Q}_{\mathrm{s}}$.

The operators (F.16) and (F.17) are finite at this point, but they do not yet show the correct behavior under charge conjugation. Each individual field operator (F.11) transforms as [530, 531]

$$\hat{\psi}^c_{\mathrm{s}}(x) := \hat{\mathscr{C}}\hat{\psi}_{\mathrm{s}}(x)\hat{\mathscr{C}}^\dagger = \eta_c C \hat{\overline{\psi}}^T_{\mathrm{s}}(x) \,, \qquad C = i\gamma^2\gamma^0 \tag{F.19}$$

(T =transposition) with an unobservable phase η_c, so that charge conjugation reorders the field operators in the current density,

$$\begin{aligned}\hat{\mathscr{C}}\hat{\overline{\psi}}_{\mathrm{s}}(x)\gamma^\mu\hat{\psi}_{\mathrm{s}}(x)\hat{\mathscr{C}}^\dagger &= \sum_{a,b,c=1}^{4} \hat{\psi}_{s,a}(x)\gamma^\mu_{ba}\gamma^0_{cb}\hat{\psi}^\dagger_{s,c}(x) \\ &= \left[\gamma^0\gamma^\mu\hat{\psi}_{\mathrm{s}}(x)\right]^T\left[\hat{\psi}^\dagger_{\mathrm{s}}(x)\right]^T .\end{aligned} \tag{F.20}$$

The proper transformation behavior of the current density operator, Eq. (8.23), thus requires the presence of both possible operator orderings, which leads to the anticommutator form (8.22). For the charge operator one then obtains

$$\hat{Q}_{\mathrm{s}} = \frac{1}{2}\int d^3x\,[\hat{\psi}^\dagger_{\mathrm{s}}(x),\hat{\psi}_{\mathrm{s}}(x)] = \frac{1}{2}\left\{\sum_{\varepsilon_k\le -m}\left[\hat{d}_k,\hat{d}_k^\dagger\right] + \sum_{-m<\varepsilon_k}\left[\hat{b}_k^\dagger,\hat{b}_k\right]\right\}. \tag{F.21}$$

This more appropriate form of $\hat{Q}_{\mathrm{s}}$ also leads to a more symmetric form of the counterterm $\langle 0_{\mathrm{s}}|\hat{Q}_{\mathrm{s}}|0_{\mathrm{s}}\rangle$ in the renormalized charge operator $\hat{Q}''_{\mathrm{s,R}}$,

$$\hat{Q}''_{\mathrm{s,R}} = \hat{Q}_{\mathrm{s}} - \langle 0_{\mathrm{s}}|\hat{Q}_{\mathrm{s}}|0_{\mathrm{s}}\rangle \qquad \langle 0_{\mathrm{s}}|\hat{Q}_{\mathrm{s}}|0_{\mathrm{s}}\rangle = \frac{1}{2}\left\{\sum_{\varepsilon_k\le -m} 1 - \sum_{-m<\varepsilon_k} 1\right\}. \tag{F.22}$$

In the case of the homogeneous vacuum with $V^\mu = 0$ each state with energy $\varepsilon_k \geq +m$ has a unique counterpart with energy $\varepsilon_k \leq -m$, so that the sums on the right hand side of (F.22) cancel each other and $\langle 0_\mathrm{s}|\hat{Q}_\mathrm{s}|0_\mathrm{s}\rangle$ vanishes.

One can proceed in a similar way for the Hamiltonian,

$$\begin{aligned}\hat{H}_\mathrm{s} &= \frac{1}{2}\int d^3x \left[\hat{\psi}_\mathrm{s}^\dagger(x), \left(-i\boldsymbol{\alpha}\cdot\boldsymbol{\nabla} + \beta m - e\alpha_\mu V^\mu(\boldsymbol{x})\right)\hat{\psi}_\mathrm{s}(x)\right] \\ &= \frac{1}{2}\left\{\sum_{\varepsilon_k\leq -m}\varepsilon_k\left[\hat{d}_k, \hat{d}_k^\dagger\right] + \sum_{-m<\varepsilon_k}\varepsilon_k\left[\hat{b}_k^\dagger, \hat{b}_k\right]\right\}. \end{aligned} \tag{F.23}$$

As the vacuum expectation value does not vanish,

$$\langle 0_\mathrm{s}|\hat{H}_\mathrm{s}|0_\mathrm{s}\rangle = \frac{1}{2}\left\{\sum_{\varepsilon_k\leq -m}\varepsilon_k - \sum_{-m<\varepsilon_k}\varepsilon_k\right\}, \tag{F.24}$$

the renormalized Hamiltonian is not identical with $\hat{H}_\mathrm{s}$,

$$\hat{H}''_{\mathrm{s,R}} := \hat{H}_\mathrm{s} - \langle 0_\mathrm{s}|\hat{H}_\mathrm{s}|0_\mathrm{s}\rangle = -\sum_{\varepsilon_k\leq -m}\varepsilon_k\hat{d}_k^\dagger\hat{d}_k + \sum_{-m<\varepsilon_k}\varepsilon_k\hat{b}_k^\dagger\hat{b}_k\,. \tag{F.25}$$

The operator (F.25) measures the energy of a given state $|\Phi\rangle$ with respect to the vacuum $|0_\mathrm{s}\rangle$ in the presence of the external potential. In the noninteracting situation these energy differences correspond directly to the "observable" ionization energies. However, the operator (F.25) does not yet reflect the fact that the vacuum energies resulting from different external potentials are not identical (Casimir effect). The differences between vacua corresponding to different V_μ are most easily seen on a local scale: the vacuum expectation value of the current density operator (8.22) reads

$$\langle 0_\mathrm{s}|\hat{j}^\mu(x)|0_\mathrm{s}\rangle = \frac{1}{2}\left\{\sum_{\varepsilon_k\leq -m}\overline{\phi}_k(\boldsymbol{x})\gamma^\mu\phi_k(\boldsymbol{x}) - \sum_{-m<\varepsilon_k}\overline{\phi}_k(\boldsymbol{x})\gamma^\mu\phi_k(\boldsymbol{x})\right\}. \tag{F.26}$$

While the net charge of the vacuum is zero, (F.26) shows the local polarization of the vacuum by the external potential. The corresponding energy difference becomes relevant as soon as the total energies associated with different external potentials are to be compared, as in the case of the HK theorem or the KS selfconsistency procedure. For such comparisons one needs a universal vacuum energy standard for which one chooses the vacuum $|0_0\rangle$ of the noninteracting system with $V^\mu = 0$, i.e. the homogeneous vacuum with $\langle 0_0|\hat{j}^\mu(x)|0_0\rangle = 0$,

$$\hat{b}_{0,k}|0_0\rangle = 0 \quad \forall\ \varepsilon_k > -m\,, \qquad \hat{d}_{0,k}|0_0\rangle = 0 \quad \forall\ \varepsilon_k \leq -m\,. \tag{F.27}$$

The corresponding field operator will be denoted by $\hat{\psi}_0$,

$$\hat{\psi}_0(x) = \sum_{\varepsilon_k\leq -m}\hat{d}_{0,k}^\dagger\phi_{0,k}(\boldsymbol{x})e^{-i\varepsilon_{0,k}t} + \sum_{-m<\varepsilon_k}\hat{b}_{0,k}\phi_{0,k}(\boldsymbol{x})e^{-i\varepsilon_{0,k}t}\,, \tag{F.28}$$

where the single-particle orbitals $\phi_{0,k}$ and eigenvalues $\varepsilon_{0,k}$ are the standard free plane-wave spinors and energies [531]. The final renormalized Hamiltonian is defined as

$$\hat{H}_{\mathrm{s,R}} := \hat{H}_{\mathrm{s}} - \langle 0_0|\hat{H}_0|0_0\rangle = \hat{H}''_{\mathrm{s,R}} + \langle 0_{\mathrm{s}}|\hat{H}_{\mathrm{s}}|0_{\mathrm{s}}\rangle - \langle 0_0|\hat{H}_0|0_0\rangle \tag{F.29}$$

$$\hat{H}_0 \;=\; \frac{1}{2}\int d^3x \left[\hat{\psi}_0^\dagger(x), \Big(-i\boldsymbol{\alpha}\cdot\boldsymbol{\nabla} + \beta m\Big)\hat{\psi}_0(x)\right]. \tag{F.30}$$

Unfortunately, there is a price to be paid for this universal definition of the energy scale. While the expectation values of (F.25) are automatically finite, the same is not true for (F.29). In order to understand the mechanism which leads to divergences, let us consider the energy of the perturbed vacuum with respect to the homogeneous vacuum (often called Casimir energy) within perturbation theory. The basic elements of the perturbation expansion are the Green's function of the perturbed vacuum,

$$iG_{\mathrm{v}}^{\mathrm{s}}(x,y) = \langle 0_{\mathrm{s}}|T\,\hat{\psi}_{\mathrm{s}}(x)\hat{\overline{\psi}}_{\mathrm{s}}(y)|0_{\mathrm{s}}\rangle \tag{F.31}$$

$$\begin{aligned} &= \Theta(x^0-y^0)\sum_{-m<\varepsilon_k}\phi_k(\boldsymbol{x})\overline{\phi}_k(\boldsymbol{y})e^{-i\varepsilon_k(x^0-y^0)} \\ &\quad -\Theta(y^0-x^0)\sum_{\varepsilon_k\le -m}\phi_k(\boldsymbol{x})\overline{\phi}_k(\boldsymbol{y})e^{-i\varepsilon_k(x^0-y^0)}, \end{aligned} \tag{F.32}$$

and its unperturbed counterpart G_{v}^0,

$$iG_{\mathrm{v}}^0(x,y) = \langle 0_0|T\,\hat{\psi}_0(x)\hat{\overline{\psi}}_0(y)|0_0\rangle \tag{F.33}$$

(the explicit form of G_{v}^0 is identical to (F.32) with ϕ_k and ε_k replaced by $\phi_{0,k}$ and $\varepsilon_{0,k}$). With these Green's functions the energy of the perturbed vacuum can be expressed as [752]

$$\begin{aligned} \langle 0_{\mathrm{s}}|\hat{H}_{\mathrm{s,R}}|0_{\mathrm{s}}\rangle \;=& -i\int d^3x \lim_{y\to x}{}_{\mathrm{s}}\,\mathrm{tr}\Big[\Big(-i\boldsymbol{\gamma}\cdot\boldsymbol{\nabla} + m + e\not{V}(\boldsymbol{x})\Big)G_{\mathrm{v}}^{\mathrm{s}}(x,y)\Big] \\ &+ i\int d^3x \lim_{y\to x}{}_{\mathrm{s}}\,\mathrm{tr}\Big[\Big(-i\boldsymbol{\gamma}\cdot\boldsymbol{\nabla} + m\Big)G_{\mathrm{v}}^0(x,y)\Big], \end{aligned} \tag{F.34}$$

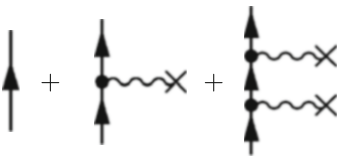
where the symmetric limit,

$$\lim_{y\to x}{}_{\mathrm{s}} \equiv \frac{1}{2}\left(\lim_{y\to x, y^0>x^0} + \lim_{y\to x, y^0<x^0}\right)\Bigg|_{(x-y)^2\ge 0}, \tag{F.35}$$

is a consequence of the anticommutator form of $\hat{H}_{\mathrm{s}}$. Similarly, one can write the current density of the perturbed vacuum as

$$\langle 0_{\mathrm{s}}|\hat{j}^\mu(x)|0_{\mathrm{s}}\rangle = -i\lim_{y\to x}{}_{\mathrm{s}}\,\mathrm{tr}\,[G_{\mathrm{v}}^{\mathrm{s}}(x,y)\gamma^\mu]\,. \tag{F.36}$$

For further analysis one can utilize a perturbation expansion of $G^{\mathrm{s}}_{\mathrm{v}}(x,y)$ in powers of the external potential, which is easily written down in terms of Feynman diagrams,

$G^{\mathrm{s}}_{\mathrm{v}} =$  $+ \cdots .$ (F.37)

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[1] (including labels)

$$iG^0_{\mathrm{v},ab}(x,y) = y,b \longrightarrow x,a \tag{F.38}$$

$$V^{\mu}(\boldsymbol{x}) = \boldsymbol{x},\mu \sim\!\!\times \tag{F.39}$$

$ie\gamma^{\mu}_{ab} =$  , (F.40)

where z represents the coordinates of the two Green's functions and the potential linked at the vertex (F.40), a,b are the spinor indices of the Green's functions and μ is the Minkowski index of the potential. As usual, integration over the coordinates and summation over the spinor and Minkowski indices attached to all internal vertices is implied in all composite diagrams as those of Eq. (F.37). After insertion of (F.37) into (F.34) and (F.36), one realizes that the symmetric limit induces so-called loop diagrams, as e.g.

$ie\langle 0_{\mathrm{s}}|\hat{j}^{\mu}(x)|0_{\mathrm{s}}\rangle =$  $+ \ldots .$ (F.41)

The evaluation of these expressions involves a loop-integration, either in real space or, after Fourier transformation, in momentum space. While the first and third diagram in (F.41) vanish (Furry's theorem), one identifies the second loop as the lowest order contribution to the vacuum polarization function (irreducible 2-point function) of standard vacuum QED (i.e. interacting fermions without external potential). This function is ultraviolet (UV) divergent, i.e. the loop integration diverges for large four momenta, when performed in momentum space. This introduces an UV-divergence in the current density and energy of the perturbed noninteracting vacuum: within a perturbative treatment it does not matter whether the external potential or the quantized photon field creates virtual electron–positron pairs. As a consequence, a UV renormalization procedure is required to keep $\langle 0_{\mathrm{s}}|\hat{H}_{\mathrm{s,R}}|0_{\mathrm{s}}\rangle$ and $\langle 0_{\mathrm{s}}|\hat{j}^{\mu}(x)|0_{\mathrm{s}}\rangle$

[1] Note that these Feynman rules follow the relativistic standard [531], rather than the nonrelativistic standard. The choice (F.38)–(F.40) avoids that additional factors of i have to be assigned to a diagram by some explicit rule.

finite. Fortunately, the corresponding counterterms are completely determined by the renormalization scheme for the Green's functions of interacting vacuum QED without external potential. We are thus led to consider standard QED in some detail, which is the subject of the next Appendix.

Appendix G
Renormalization Scheme of Vacuum QED

In this Appendix we review the renormalization scheme of vacuum QED without external potential, i.e. of the Lagrangian (8.11) with

$$V^{\mu}(\boldsymbol{x}) = 0 \tag{G.1}$$

and the system being in the state with zero net charge. This summary not only serves as an introduction of the basic concepts of UV renormalization, as e.g. the counterterm technique, but also provides a number of explicit results used in the Appendices H and I. In fact, all counterterms required for inhomogeneous systems with non-vanishing current density can be extracted from the study of the vacuum Green's functions of QED without external potential: neither the presence of a perturbing external potential nor that of bound electrons introduces any new feature or new parameter. An explicit illustration of this statement has already been given in Eq. (F.41) for the case of a noninteracting inhomogeneous system. Further examples will turn up in the analysis of the homogeneous and the weakly inhomogeneous electron gas in the Appendices H and I, which also provide the background for the discussion of the existence theorem of relativistic DFT in Sect. 8.3. For brevity, we use $\hbar = c = 1$ in this and the other Appendices dealing with relativistic many-body theory.

The basic vacuum Green's functions to which we restrict the subsequent discussion are the fermion and photon propagators as well as the (reducible) vertex function,

$$G_{\mathrm{v}}(x,y) = -i\langle 0|T\,\hat{\psi}(x)\hat{\bar{\psi}}(y)|0\rangle \tag{G.2}$$

$$D_{\mathrm{v}}^{\mu\nu}(x,y) = -i\langle 0|T\hat{A}^{\mu}(x)\hat{A}^{\nu}(y)|0\rangle \tag{G.3}$$

$$G_{\mathrm{v}}^{(2,1)\mu}(x,y,z) = -\langle 0|T\,\hat{\psi}(x)\hat{\bar{\psi}}(y)\hat{A}^{\mu}(z)|0\rangle\,, \tag{G.4}$$

where $|0\rangle$ denotes the vacuum of the interacting theory. Note that we have defined the photon propagator without any prefactor of e^2, which is most suitable for the discussion of renormalization (but differs from the definitions (8.83) and (H.8) which are more adequate for the discussion of RDFT).

The standard approach to the calculation of such Green's functions is perturbation theory with respect to the electron–electron coupling constant $\alpha = e^2/(\hbar c)$. This procedure results in an expansion of the vacuum Green's functions of the interacting system in terms of vacuum expectation values of the noninteracting field operators $\hat{\psi}_0$ and $\hat{A}_0^\mu$ (see e.g. [531]). For instance, for the electron propagator one obtains

$$G_{\rm v}(x-y) = -i\frac{\langle 0_0|T\,\hat{\psi}_0(x)\hat{\overline{\psi}}_0(y)\exp[ie\int d^4z\,\hat{\overline{\psi}}_0(z)\hat{\not{A}}_0(z)\hat{\psi}_0(z)]|0_0\rangle}{\langle 0_0|T\exp[ie\int d^4z\,\hat{\overline{\psi}}_0(z)\hat{\not{A}}_0(z)\hat{\psi}_0(z)]|0_0\rangle}\,, \tag{G.5}$$

where $|0_0\rangle$ is the noninteracting vacuum introduced in Eq. (F.27). In addition, the Feynman dagger notation,

$$\not{A} = A_\mu\gamma^\mu\,, \tag{G.6}$$

has been used. Analogous expressions are obtained for $D_{\rm v}^{\mu\nu}$ and $G_{\rm v}^{(2,1)\mu}$. The actual expansion of all vacuum expectation values of the type (G.5) in powers of e^2 is controlled by the Feynman rules resulting from the application of Wick's theorem. The basic ingredients are the noninteracting fermion propagator $G_{\rm v}^0$, Eq. (F.33), the noninteracting photon propagator $D_{\mu\nu}^0$, Eq. (8.83), and the bare fermion-photon vertex (F.40) (together with the loop integrations and the fermion loop sign rule). It is this perturbative framework in which the concept of renormalization is usually formulated and we follow this standard.

Due to the translational invariance of QED without external potential, the situation is most conveniently analyzed in momentum space. The corresponding four-dimensional Fourier transforms can be written as

$$G_{\rm v}(x-y) = \int\frac{d^4p}{(2\pi)^4}\,e^{-ip\cdot(x-y)}\,G_{\rm v}(p) \tag{G.7}$$

$$D_{\rm v}^{\mu\nu}(x-y) = \int\frac{d^4q}{(2\pi)^4}\,e^{-iq\cdot(x-y)}\,D_{\rm v}^{\mu\nu}(q) \tag{G.8}$$

$$G_{{\rm v},\mu}^{(2,1)}(x,y,z) = \int\frac{d^4p}{(2\pi)^4}\frac{d^4k}{(2\pi)^4}\,e^{-ip\cdot(x-z)-ik\cdot(z-y)}\,G_{{\rm v},\mu}^{(2,1)}(p,k)\,. \tag{G.9}$$

This leads to loop integrations over four momenta rather than space-time coordinates (as in (G.5)), with four momentum conservation at the vertices. In momentum space the noninteracting propagator $G_{\rm v}^0$, Eq. (F.33), is given by

$$i\,G_{\rm v}^0(p) = i\,\frac{p+m}{p^2-m^2+i\eta} = \xrightarrow{\;p\;}\,. \tag{G.10}$$

As discussed in Sect. 8.2 the form of the free photon propagator $D_{\mu\nu}^0(q)$ depends on the choice of gauge. In Sects. 8.3–8.7 Feynman gauge ($\lambda = 1$) is used, for which $D_{\mu\nu}^0$ is explicitly given by

$$D^0_{\mu\nu}(q) = D^0(q^2)\, g_{\mu\nu} \tag{G.11}$$

$$D^0(q^2) = \frac{-4\pi}{q^2 + i\eta}\,. \tag{G.12}$$

For the present purpose, however, Landau gauge is more adequate, which corresponds to the choice $\lambda = \infty$,

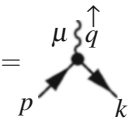
$$iD^0_{\mu\nu}(q) = i\left(g_{\mu\nu} - \frac{q_\mu q_\nu}{q^2}\right) D^0(q^2) = \quad \mu \overset{q}{\sim\!\sim} \nu \quad . \tag{G.13}$$

It seems worthwhile to emphasize that all covariant gauges can be handled by the same basic renormalization scheme. As $\langle 0_0 | T\, \hat{\psi}_0(x) \bar{\hat{\psi}}_0(y) \hat{A}^\mu_0(z) | 0_0 \rangle = 0$, the first non-vanishing contribution to $G^{(2,1)\mu}_{\rm v}$ is found in first order of e,

$$G^{(2,1)}_{{\rm v},\mu}(p,k) = -D^0_{\mu\nu}(p-k) G^0_{\rm v}(p) e\gamma^\nu G^0_{\rm v}(k)\,. \tag{G.14}$$

Its core element is the simple vertex (F.40) in momentum space,

$$ie\gamma^\mu (2\pi)^4 \delta^{(4)}(p-k-q) = \tag{G.15}$$



(the arrow above q indicates that this four momentum is supposed to be outgoing from the vertex, so that the argument of the δ-function is the sum over all incoming four momenta—in momentum space a direction has to be assigned to each interaction line).

In the first step of the analysis the relevant Green's functions are expressed in terms of their irreducible kernels [753], the electron self-energy $\Sigma_{\rm v}(p)$, the vacuum polarization tensor $\omega_{{\rm v},\mu\nu}(q)$ and the irreducible vertex function $\Gamma_{{\rm v},\mu}(p,k)$. The connection between these quantities is provided by Dyson equations (see e.g. [531]),

$$G_{\rm v}(p) = G^0_{\rm v}(p) + G^0_{\rm v}(p)\, \Sigma_{\rm v}(p)\, G_{\rm v}(p) \tag{G.16}$$

$$D_{{\rm v},\mu\nu}(q) = D^0_{\mu\nu}(q) + D^0_{\mu\rho}(q)\, \omega^{\rho\lambda}_{\rm v}(q)\, D_{{\rm v},\lambda\nu}(q) \tag{G.17}$$

$$G^{(2,1)}_{{\rm v},\mu}(p,k) = -e D_{{\rm v},\mu\nu}(p-k)\, G_{\rm v}(p)\, [\gamma^\nu + \Gamma^\nu_{\rm v}(p,k)]\, G_{\rm v}(k)\,. \tag{G.18}$$

The relations (G.16)–(G.18) separate the nontrivial higher order contributions in the perturbation expansions from trivial multiples of lower order terms, thus isolating the essential information contained in the Green's functions. These relations become particularly simple if (G.16) is rewritten in terms of inverse propagators,

$$G_{\rm v}(p)^{-1} = G^0_{\rm v}(p)^{-1} - \Sigma_{\rm v}(p) = \not{p} - m - \Sigma_{\rm v}(p)\,, \tag{G.19}$$

and if the tensor structure of $\omega^{\mu\nu}_{\rm v}(q)$,

$$\omega_{\rm v}^{\mu\nu}(q) = \left(q^2 g^{\mu\nu} - q^\mu q^\nu\right) \omega_{\rm v}(q^2)\,, \tag{G.20}$$

is used in (G.17),

$$D_{\rm v}^{\mu\nu}(q) = \left(g^{\mu\nu} - \frac{q^\mu q^\nu}{q^2}\right) \frac{-4\pi}{q^2[1+4\pi\omega_{\rm v}(q^2)]}\,. \tag{G.21}$$

The renormalization program of QED starts with and is most easily illustrated for the first order. The lowest order contributions to the three relevant irreducible 2- and 3-point functions read

$$-i\Sigma_{\rm v}^{(1)}(p) = \quad p-q \quad q$$

$$= e^2 \int \frac{d^4q}{(2\pi)^4} D^0_{\mu\nu}(q)\, \gamma^\mu\, G^0_{\rm v}(p-q)\, \gamma^\nu \tag{G.22}$$

$$-i\omega^{(1)}_{{\rm v},\mu\nu}(q) = \quad \nu \quad p \quad p-q \quad \mu$$

$$= -e^2 \int \frac{d^4p}{(2\pi)^4} \,{\rm tr}\left[\gamma_\mu\, G^0_{\rm v}(p)\, \gamma_\nu\, G^0_{\rm v}(p-q)\right] \tag{G.23}$$

$$ie\Gamma^{(1)}_{{\rm v},\mu}(p,k) = \quad k-q \quad \mu \quad q \quad p-q$$

$$= -e^3 \int \frac{d^4q}{(2\pi)^4} D^0_{\rho\nu}(q)\gamma^\rho\, G^0_{\rm v}(p-q)\gamma_\mu G^0_{\rm v}(k-q)\gamma^\nu. \tag{G.24}$$

Insertion of (G.10), (G.13) shows that these integrals diverge for large loop (four) momentum. As these divergences result from the high energy regime they are called UV-divergences—for brevity we ignore all problems related to the infrared (low energy) regime. In order to establish a well-defined theory one first of all needs a regularization scheme which suppresses these divergences at all intermediate steps of the evaluation. Of course, this regularization must preserve the complete structure of the theory, in particular the Ward-Takahashi identities, which link the irreducible kernels (see e.g. [531]), as for example

$$(p_\mu - p'_\mu)\Gamma^\mu_{\rm v}(p,p') = \Sigma_{\rm v}(p') - \Sigma_{\rm v}(p) \tag{G.25}$$

$$\Longrightarrow \qquad \Gamma^{\mu}_{\mathrm{v}}(p,p) = -\frac{\partial}{\partial p_\mu}\Sigma_{\mathrm{v}}(p)\,. \tag{G.26}$$

For the present discussion we use dimensional regularization [754], in which all integrals of the type (G.22)–(G.24) are evaluated in a reduced number of d dimensions, rather than the 4-dimensional Minkowski space (after Wick rotation in order to obtain integrals in Euclidean space—the details of this scheme are not relevant at this point). The results evaluated for integer d are then analytically continued to non-integer d, which then allows their extension to the physically interesting limit $d \to 4$. Using the abbreviation $\Delta = (4-d)/2$ one finds for the integrals (G.22)–(G.24)

$$\Sigma^{(1)}_{\mathrm{v}}(p) = \frac{e^2}{4\pi}\Gamma(\Delta)(-\not{p}+4m) + \Sigma^{(1)}_{\mathrm{v,finite}}(p) \tag{G.27}$$

$$\omega^{(1)}_{\mathrm{v},\mu\nu}(q) = (q^2 g_{\mu\nu} - q_\mu q_\nu)\left(\frac{e^2}{12\pi^2}\Gamma(\Delta) + \omega^{(1)}_{\mathrm{v,finite}}(q^2)\right) \tag{G.28}$$

$$\Gamma^{(1)}_{\mathrm{v},\mu}(p,k) = \frac{e^2}{4\pi}\Gamma(\Delta)\gamma_\mu + \Gamma^{(1)}_{\mathrm{v,finite},\mu}(p,k)\,. \tag{G.29}$$

Here $\Gamma(\Delta)$ denotes Euler's Γ-function, in which the UV-divergences have been isolated,

$$\Gamma(\Delta) \stackrel{\Delta\to 0}{\longrightarrow} \frac{1}{\Delta} + \dots\ ,$$

and $\Sigma^{(1)}_{\mathrm{v,finite}}$, $\omega^{(1)}_{\mathrm{v,finite}}$ and $\Gamma^{(1)}_{\mathrm{v,finite},\mu}$ represent the finite parts of the irreducible kernels in which the limit $d \to 4$ can be taken directly (the detailed form of $\Sigma^{(1)}_{\mathrm{v,finite}}$, $\omega^{(1)}_{\mathrm{v,finite}}$ and $\Gamma^{(1)}_{\mathrm{v,finite},\mu}$ is not relevant in this context). The UV-divergences now manifest themselves as simple poles in the deviation of the space-time dimensionality from $d = 4$. On the other hand, all other irreducible n-point functions are finite from the very outset (to first order).

The next step is the actual renormalization procedure. The crucial observation for both the physical interpretation as well as the technical success of this step is the fact that the divergent contributions to the three relevant functions have the same structure as the corresponding free propagators and the free vertex: the divergent part of $\Sigma^{(1)}_{\mathrm{v}}$ is just proportional to $\not{p}$ and m, but not e.g. to p^2, the divergent part of $\omega^{(1)}_{\mathrm{v},\mu\nu}$ has the same tensor structure as $D^0_{\mu\nu}$, Eq. (G.13), and the divergent part of $\Gamma^{(1)}_{\mathrm{v},\mu}$ is proportional to the free vertex γ_μ (but does not depend on momentum). For this reason the divergences can be absorbed into a redefinition of the constants m and e as well as a modified normalization of the field operators in the original Lagrangian. Given the form of this original, unrenormalized Lagrangian, $\mathscr{L}_{\mathrm{unren}}(\hat{\psi},\hat{A}^\mu,m,e)$, the renormalized Lagrangian is usually written as

$$\mathscr{L}_{\mathrm{R}} = \mathscr{L}_{\mathrm{unren}}\left(\sqrt{Z_2}\hat{\psi}, \sqrt{Z_3}\hat{A}^\mu, m-\delta m, \frac{Z_1 e}{Z_2\sqrt{Z_3}}\right). \tag{G.30}$$

The renormalization constants Z_1, Z_2, Z_3 and δm have to be interpreted as functions of the finite true physical charge e and mass m of the electrons. The relation between these quantities remains to be determined order by order in the perturbation series. In other words: the original fields and parameters in $\mathscr{L}_{\text{unren}}$ are no longer interpreted as the correct physical fields and parameters, but rather as bare, unrenormalized quantities,

$$\hat{\psi}_b(x) = \sqrt{Z_2}\hat{\psi}(x) \tag{G.31}$$

$$\hat{A}^\mu_b(x) = \sqrt{Z_3}\hat{A}^\mu(x) \tag{G.32}$$

$$e_b = \frac{Z_1}{Z_2\sqrt{Z_3}}\, e \tag{G.33}$$

$$m_b = m - \delta m\,, \tag{G.34}$$

so that the renormalized Lagrangian can be reformulated in terms of the bare quantities,

$$\mathscr{L}_{\text{R}} = \mathscr{L}_{\text{unren}}(\hat{\psi}_b, \hat{A}^\mu_b, m_b, e_b)\,. \tag{G.35}$$

The structure of the theory, which e.g. expresses itself in Dyson equations and Ward-Takahashi identities, remains completely unchanged, due to the form invariance of the Lagrangian under the renormalization prescription. The renormalized Green's functions, i.e. the vacuum expectation values of $\hat{\psi}$ and $\hat{A}^\mu$, are now obtained as

$$\begin{aligned} G_{\text{v,R}}(x,y) &= -iZ_2^{-1}\langle 0|T\,\hat{\psi}_b(x)\bar{\hat{\psi}}_b(y)|0\rangle \\ &= Z_2^{-1}G_{\text{v}}(x,y,e_b,m_b) \end{aligned} \tag{G.36}$$

$$\begin{aligned} D^{\mu\nu}_{\text{v,R}}(x,y) &= -iZ_3^{-1}\langle 0|T\hat{A}^\mu_b(x)\hat{A}^\nu_b(y)|0\rangle \\ &= Z_3^{-1}D^{\mu\nu}_{\text{v}}(x,y,e_b,m_b) \end{aligned} \tag{G.37}$$

$$\begin{aligned} G^{(2,1)\mu}_{\text{v,R}}(x,y,z) &= -Z_2^{-1}Z_3^{-1/2}\langle 0|T\,\hat{\psi}_b(x)\bar{\hat{\psi}}_b(y)\hat{A}^\mu_b(z)|0\rangle \\ &= Z_2^{-1}Z_3^{-1/2}G^{(2,1)\mu}_{\text{v}}(x,y,z,e_b,m_b)\,. \end{aligned} \tag{G.38}$$

In these relations it has been indicated explicitly that the unrenormalized Green's functions resulting from the Lagrangian (G.35) initially depend on the bare parameters e_b and m_b.

In order to determine the unknown renormalization constants one needs some normalization conditions. These conditions result from the basic physical requirements for the Green's functions: in order to describe real fermions, which satisfy the dispersion relation $p^2 = (p^0)^2 - \boldsymbol{p}^2 = m^2$ with the finite experimental mass m in the presence of the virtual photon cloud, $G_{\text{v,R}}(p)$ should reduce to the form of the free propagator $G^0_{\text{v}}(p)$ with physical mass m for on-shell momentum $p^2 = m^2$, i.e. should have a simple pole with residue 1 for $p^2 = m^2$. If Σ_{v} is expressed as a function of $\not{p} - m$ (using $\not{p}^2 = p^2$) and the physical parameters,

$$\Sigma_{\rm v}(p,e_b,m_b) = \sum_{n=0}^{\infty} \Sigma_n(e,m)(\not{p}-m)^n\,, \tag{G.39}$$

the renormalized inverse propagator can be written as

$$G^{-1}_{\rm v,R}(p) = Z_2\Bigg[\delta m - \Sigma_0(e,m) + (\not{p}-m)(1-\Sigma_1(e,m)) - \sum_{n=2}^{\infty}\Sigma_n(e,m)(\not{p}-m)^n\Bigg]\,. \tag{G.40}$$

For $G_{\rm v,R}(p)$ to have a simple pole at $p^2=m^2$, however, one must have

$$\delta m = \Sigma_0(e,m) = \Sigma_{\rm v}(p,e_b,m_b)\Big|_{\not{p}=m} \tag{G.41}$$

$$Z_2 = (1-\Sigma_1(e,m))^{-1} = \left(1-\frac{d}{d\not{p}}\Sigma_{\rm v}(p,e_b,m_b)\Big|_{\not{p}=m}\right)^{-1}. \tag{G.42}$$

Only this choice guarantees that the higher order terms in the propagator itself are finite for $p^2=m^2$. In fact, insertion of (G.19), (G.39), (G.41) and (G.42) into (G.36) yields

$$\begin{aligned}
G_{\rm v,R}(p) &= \left[Z_2\left(G^0_{\rm v}(p,m_b)^{-1} - \Sigma_{\rm v}(p,e_b,m_b)\right)\right]^{-1} \\
&= \left[G^0_{\rm v}(p,m)^{-1}\left(1 - G^0_{\rm v}(p,m)Z_2\sum_{n=2}^{\infty}\Sigma_n(e,m)(\not{p}-m)^n\right)\right]^{-1} \\
&= \sum_{k=0}^{\infty}\left(G^0_{\rm v}(p,m)Z_2\sum_{n=2}^{\infty}\Sigma_n(e,m)(\not{p}-m)^n\right)^k G^0_{\rm v}(p,m) \\
&= \frac{\not{p}+m}{p^2-m^2} + \frac{\not{p}+m}{p^2-m^2}\left[Z_2\sum_{n=2}^{\infty}\Sigma_n(e,m)(\not{p}-m)^n\right]\frac{\not{p}+m}{p^2-m^2} + \dots \\
&= \frac{\not{p}+m}{p^2-m^2} + \left[Z_2\sum_{n=2}^{\infty}\Sigma_n(e,m)(\not{p}-m)^{n-2}\right] + \dots\,.
\end{aligned}$$

Given the renormalized Green's functions, one can also define the corresponding renormalized irreducible kernels,

$$G^{-1}_{\rm v,R}(p) = \not{p} - m - \Sigma_{\rm v,R}(p)\,. \tag{G.43}$$

The additional contributions to the renormalized Green's functions resulting from renormalization are usually called counterterms. From Eqs. (G.40), (G.43) one extracts as counterterms to the self-energy,

$$\Sigma_{\rm v,R}(p) = \Sigma_{\rm v}(p) + \Delta\Sigma_{\rm v}(p)\,, \qquad \Delta\Sigma_{\rm v}(p) = -Z_2\delta m + (1-Z_2)(\not{p}-m)\,, \tag{G.44}$$

so that $\Sigma_{\mathrm{v,R}}$ satisfies the normalization conditions

$$\Sigma_{\mathrm{v,R}}(p)\Big|_{\not{p}=m} = 0\,, \qquad \frac{d}{d\not{p}}\Sigma_{\mathrm{v,R}}(p)\Big|_{\not{p}=m} = 0\,, \tag{G.45}$$

which should be interpreted in the spirit of the expansion (G.39) as

$$\Sigma_{0,\mathrm{R}}(e,m) = \Sigma_{1,\mathrm{R}}(e,m) = 0\,.$$

One proceeds in the same fashion for the other two divergent functions. In the case of the massless photons the renormalized propagator must have a simple pole at $q^2 = 0$, which allows the determination of Z_3. Combination of (G.37) with (G.21) leads to

$$D^{\mu\nu}_{\mathrm{v,R}}(q) = \left(g^{\mu\nu} - \frac{q^\mu q^\nu}{q^2}\right)\frac{-4\pi}{q^2[1+4\pi\omega_{\mathrm{v,R}}(q^2)]}\,, \tag{G.46}$$

with $\omega_{\mathrm{v,R}}$ defined by

$$1+4\pi\omega_{\mathrm{v,R}}(q^2) = Z_3\left[1+4\pi\omega_{\mathrm{v}}(q^2,e_b,m_b)\right]\,. \tag{G.47}$$

The zero mass pole requirement is thus satisfied, if

$$Z_3 \;=\; \Big[1+4\pi\omega_{\mathrm{v}}(q^2=0,e_b,m_b)\Big]^{-1} \quad\Longleftrightarrow\quad \omega_{\mathrm{v,R}}(q^2=0) = 0\,. \tag{G.48}$$

Consistent with Eq. (G.20), one then defines the renormalized irreducible polarization tensor as

$$\omega^{\mu\nu}_{\mathrm{v,R}}(q) \;=\; \left(q^2 g^{\mu\nu} - q^\mu q^\nu\right)\omega_{\mathrm{v,R}}(q^2)\,. \tag{G.49}$$

Finally, the renormalized irreducible vertex function is defined via the Dyson equation (G.18),

$$G^{(2,1)}_{\mathrm{v,R},\mu}(p,k) \;=\; -eD_{\mathrm{R},\mu\nu}(p-k)G_{\mathrm{v,R}}(p)\left[\gamma^\nu + \Gamma^\nu_{\mathrm{v,R}}(p,k)\right]G_{\mathrm{v,R}}(k)\,, \tag{G.50}$$

using the renormalized propagators (G.36), (G.37). Combination of (G.50) with (G.38) and (G.33) then leads to

$$e\left[\gamma^\mu + \Gamma^\mu_{\mathrm{v,R}}(p,k)\right] \;=\; Z_1 e\left[\gamma^\mu + \Gamma^\mu_{\mathrm{v}}(p,k,e_b,m_b)\right]\,, \tag{G.51}$$

which allows the formulation of a normalization condition for Z_1. On the mass shell, $\not{p} = m$, the vertex function must reduce to a pure vertex with physical charge e, in order to reproduce the Coulomb interaction for well separated electrons,

$$\gamma^\mu \;=\; Z_1\left(\gamma^\mu + \Gamma^\mu_{\mathrm{v}}(p,p,e_b,m_b)\Big|_{\not{p}=m}\right) \quad\Longleftrightarrow\quad \Gamma^\mu_{\mathrm{v,R}}(p,p)\Big|_{\not{p}=m} = 0\,. \tag{G.52}$$

Using the Ward-Takahashi identity (G.26) and the expansion (G.39), one can explicitly verify that the resulting Z_1,

$$Z_1 = \left[1 + \frac{1}{4}\gamma_\mu \Gamma_{\rm v}^\mu(p,p,e_b,m_b)\Big|_{\not p = m}\right]^{-1}, \tag{G.53}$$

is identical with Z_2, Eq. (G.42).

As perturbation theory on the basis of (G.35) yields the irreducible functions in terms of the bare parameters, the expressions on the right-hand sides of (G.41), (G.42), (G.48) and (G.53) are obtained by use of (G.33) and (G.34), so that they themselves depend on the renormalization constants. Renormalization thus has to proceed in a recursive fashion, i.e. order by order in perturbation theory.

Explicit results are easily obtained for the first order. Use of (G.27), (G.40) gives

$$\begin{aligned} G^{(1)}_{\rm v,R}(p)^{-1} = Z_2 \Bigg[\not p \left(1 + \frac{e_b^2}{4\pi}\Gamma(\Delta)\right) - m_b \left(1 + \frac{e_b^2}{\pi}\Gamma(\Delta)\right) \\ - \Sigma^{(1)}_{\rm v,finite}(p,e_b,m_b)\Bigg]. \end{aligned} \tag{G.54}$$

One now expands the right-hand side of (G.54) consistently to first order, using $Z_2 = 1 + Z_2^{(1)} + \ldots$ and $m_b = m - \delta m^{(1)} + \ldots$,

$$\begin{aligned} G^{(1)}_{\rm v,R}(p)^{-1} = \delta m^{(1)} - \frac{3e^2}{4\pi}\Gamma(\Delta)m + (\not p - m)\left(1 + \frac{e^2}{4\pi}\Gamma(\Delta) + Z_2^{(1)}\right) \\ - \Sigma^{(1)}_{\rm v,finite}(p,e,m). \end{aligned} \tag{G.55}$$

The conditions (G.41), (G.42) or, alternatively, (G.45), then give

$$\delta m^{(1)} = \frac{3e^2}{4\pi}\Gamma(\Delta)m + \Sigma^{(1)}_{\rm v,finite}(p,e,m)\Big|_{\not p = m} \tag{G.56}$$

$$Z_2^{(1)} = -\frac{e^2}{4\pi}\Gamma(\Delta) + \frac{d}{d\not p}\Sigma^{(1)}_{\rm v,finite}(p,e,m)\Big|_{\not p = m}. \tag{G.57}$$

From Eqs. (G.44), (G.56), (G.57) one extracts as first order counterterm to the self-energy,

$$\begin{aligned} \Delta\Sigma^{(1)}_{\rm v}(p) = -\frac{3e^2}{4\pi}\Gamma(\Delta)m - \Sigma^{(1)}_{\rm v,finite}(p,e,m)\Big|_{\not p = m} \\ + \left[\frac{e^2}{4\pi}\Gamma(\Delta) - \frac{d}{d\not p}\Sigma^{(1)}_{\rm v,finite}(p,e,m)\Big|_{\not p = m}\right](\not p - m). \end{aligned} \tag{G.58}$$

Similarly, $Z_3 = 1 + Z_3^{(1)} + \ldots$ is determined by (G.28) and (G.48)

$$Z_3^{(1)} = -\frac{e^2}{3\pi}\Gamma(\Delta) \qquad \left(\omega^{(1)}_{\rm v,finite}(q^2 = 0) = 0\right). \tag{G.59}$$

The associated counterterm for $\omega^{(1)}_{\mathrm{v},\mu\nu}$ results from (G.47) and (G.49),

$$\Delta\omega^{(1)}_{\mathrm{v},\mu\nu}(q) = -(q^2 g_{\mu\nu} - q_\mu q_\nu)\frac{e^2}{12\pi^2}\Gamma(\Delta)\,. \tag{G.60}$$

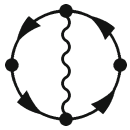
Finally, the vertex correction is renormalized by

$$\Delta\Gamma^{(1)}_{\mathrm{v},\mu}(p,k) = Z_1^{(1)}\gamma_\mu \tag{G.61}$$

$$Z_1^{(1)} = -\frac{e^2}{4\pi}\Gamma(\Delta) - \frac{1}{4}\gamma^\mu \Gamma^{(1)}_{\mathrm{v,finite},\mu}(p,p,e,m)\Big|_{\not{p}=m}\,. \tag{G.62}$$

At this point, all Green's functions are finite to first order. At the same time, all symmetries of the theory have been preserved, which may be checked by verification of (G.26) for the renormalized functions.

This procedure can be repeated for all higher orders of perturbation theory [531], after discussion of overlapping divergences, which occur for instance in the diagram



Note that all artificial divergences resulting from use of e_b and m_b inside the finite parts of the Green's functions or from multiplication of finite terms with $Z_1^{(1)}$ etc are eliminated by higher order contributions to the renormalization constants. No further details are given at this point, as the first order provides all explicit results required for our discussion of RDFT.

The final form of the renormalized Lagrangian of QED is

$$\begin{aligned}\mathscr{L}_{\mathrm{R}} = {} & Z_2\hat{\bar{\psi}}(x)\Big(i\not{\partial} - m + \delta m + e\not{V}(\boldsymbol{x}) + e\not{\hat{A}}(x)\Big)\hat{\psi}(x) \\ & - \frac{Z_3}{16\pi}\hat{F}_{\mu\nu}(x)\hat{F}^{\mu\nu}(x) - \frac{Z_3\lambda}{8\pi}\Big(\partial_\nu \hat{A}^\nu(x)\Big)^2\,,\end{aligned} \tag{G.63}$$

where we have now reintroduced the external potential V^μ in order to indicate that it has to be renormalized in the same spirit as the quantized photon field: this is immediately obvious if one analyzes the Lagrangian (G.63) in terms of perturbation theory with respect to V^μ. The renormalization constants are thus uniquely determined by vacuum QED without any external potential, so that they do not depend on the specific V^μ present. If one bases the perturbation expansion on the Lagrangian (G.63) all vacuum Green's and n-point functions of the theory (defined in terms of the physical fields $\hat{\psi}$ and $\hat{A}^\mu$) are UV finite.

Appendix H
Relativistic Homogeneous Electron Gas

In this Appendix we summarize some properties of the relativistic homogeneous electron gas (RHEG) in order to illustrate the renormalization of ground state energies (indicated in Sect. 8.2) and to provide the background for the RLDA (Sect. 8.8.3) as well as for the relativistic gradient expansion (Appendix J). For simplicity we restrict the discussion to the unpolarized RHEG (for details of the polarized RHEG see [546] and references therein).

The basic concept of the RHEG follows that of the HEG, introduced in Sect. 4.3—the RHEG consists of an infinite electron gas with density n_0 plus a neutralizing positive background charge density $n_+ = n_0$, which suppresses long-range Coulomb divergences. Now, however, the electrons and their interaction are treated on the level of the QED, i.e. the Lagrangian (8.11) with $V^\mu = 0$.

As in the preceding Appendix we use $\hbar = c = 1$.

H.1 Basic Propagators

We start by noting the basic differences between the perturbative treatment of the RHEG and that of vacuum QED, discussed in Appendix G. While the Hamiltonian of the RHEG, $\hat{H}^{\mathrm{hom}}$, is identical to that of vacuum QED, the ground state $|\Psi_0\rangle$ of the RHEG represents a gas of electrons with finite density n_0, in contrast to the ground state $|0\rangle$ of vacuum QED. As a consequence the fermion propagator,

$$G(x,y) = -i\langle\Psi_0|T\,\hat{\psi}(x)\bar{\hat{\psi}}(y)|\Psi_0\rangle\,, \tag{H.1}$$

differs from G_{v} already on the noninteracting level. In momentum space the noninteracting fermion propagator of the RHEG is given by

$$G^0(p) = G^0_{\mathrm{v}}(p) + G^0_{\mathrm{d}}(p) \;=\; G_-(p) + G_+(p) \tag{H.2}$$

$$G^0_{\mathrm{d}}(p) = 2\pi i\delta(p^0 - E_p)\,\frac{\not{p}+m}{2E_p}\,\Theta(k_{\mathrm{F}} - |\boldsymbol{p}|) \tag{H.3}$$

$$G_-(p) = \frac{\not{p}_- + m}{2E_p} \frac{-1}{p^0 + E_p - i\eta} \tag{H.4}$$

$$G_+(p) = \frac{\not{p}_+ + m}{2E_p} \left[\frac{\Theta(|\boldsymbol{p}| - k_\mathrm{F})}{p^0 - E_p + i\eta} + \frac{\Theta(k_\mathrm{F} - |\boldsymbol{p}|)}{p^0 - E_p - i\eta} \right], \tag{H.5}$$

where $E_p = \sqrt{\boldsymbol{p}^2 + m^2}$, $p^\mu_\pm = (\pm E_p, p^i)$ and the Fermi momentum k_F is related to the electron density n_0 of the RHEG as in the nonrelativistic case,

$$n_0 = \frac{k_\mathrm{F}^3}{3\pi^2}\,. \tag{H.6}$$

Two alternative forms for G^0 have been listed, the first one emphasizes its relation to the vacuum propagator $G^0_\mathrm{v}(p)$, Eq. (G.10), the second one indicates its decomposition into positive energy (G_+) and negative energy (G_-) contributions. In the nonrelativistic limit the upper left part of the matrix $G_+(p^0 + m, \boldsymbol{p})$ goes over into the standard nonrelativistic electron gas propagator. Note that due to charge conservation the density of the RHEG is not changed by switching on the electron–electron interaction, so that n_0 also represents the density of the interacting RHEG. Equation (H.6) thus also relates the interacting density to the noninteracting k_F. Diagrammatically the full $G^0(p)$, Eq. (H.2), will be represented by

$$iG^0(p) = \tag{H.7}$$

in the following. The other two basic elements of perturbation theory, the noninteracting photon propagator and the simple vertex, remain unchanged. However, it seems worth pointing out that the full photon propagator

$$D_{\mu\nu}(x,y) = -ie^2 \langle \Psi_0 | T \hat{A}_\mu(x) \hat{A}_\nu(y) | \Psi_0 \rangle\,, \tag{H.8}$$

and the full vertex function do not: in the case of the RHEG not only virtual electron-positron pairs screen the bare interaction but also virtual electron-hole pairs. Note that we have introduced an additional factor of e^2 in the definition (H.8), as compared with the definition (G.3). This reflects the fact that it is more convenient for the subsequent discussion that the corresponding free propagator $D^0_{\mu\nu}$ approaches the Coulomb interaction in the limit $c \to \infty$.

H.2 Response Functions

Most information on the RHEG which is required in the present context is contained in the response functions of the RHEG. In our notation the time-ordered current response functions (n-point functions) are defined as

$$\chi^{(n)}_{\mu_1 \ldots \mu_n}(x_1, \ldots x_n) := (-i)^{n-1} \langle \Psi_0 | T \delta \hat{j}_{\mu_1}(x_1) \ldots \delta \hat{j}_{\mu_n}(x_n) | \Psi_0 \rangle\,, \tag{H.9}$$

with the operator $\delta\hat{j}_\mu$ for the induced current given by

$$\delta\hat{j}_\mu(t,\boldsymbol{r}) = \hat{j}_\mu(t,\boldsymbol{r}) - \langle\Psi_0|\hat{j}_\mu(t,\boldsymbol{r})|\Psi_0\rangle = \hat{j}_\mu(t,\boldsymbol{r}) - j_\mu(\boldsymbol{r})\,. \tag{H.10}$$

For the time-independent systems of interest here a partial Fourier transformation of $\chi^{(n)}_{\mu_1\ldots\mu_n}$ is advantageous,

$$\begin{aligned}\chi^{(n)}_{\mu_1\ldots\mu_n}(t_1,\boldsymbol{r}_1;\ldots t_n,\boldsymbol{r}_n) = \int\frac{d\omega_1}{2\pi}\cdots\int\frac{d\omega_n}{2\pi}\; e^{-i\omega_1 t_1\ldots-i\omega_n t_n}\\ \times 2\pi\delta(\omega_1+\ldots+\omega_n)\\ \times\chi^{(n)}_{\mu_1\ldots\mu_n}(\omega_1,\boldsymbol{r}_1;\ldots\omega_n,\boldsymbol{r}_n)\,.\end{aligned} \tag{H.11}$$

The static response functions utilized in Appendix I are then obtained by taking the zero-frequency limit,

$$\chi^{(n)}_{\mu_1\ldots\mu_n}(\boldsymbol{r}_1,\ldots\boldsymbol{r}_n) \equiv \chi^{(n)}_{\mu_1\ldots\mu_n}(\omega_1=0,\boldsymbol{r}_1;\ldots\omega_n=0,\boldsymbol{r}_n)\,. \tag{H.12}$$

For the case of the RHEG further Fourier transformation is useful,

$$\begin{aligned}\chi^{(n)}_{\mu_1\ldots\mu_n}(q^0_1,\boldsymbol{r}_1;\ldots q^0_n,\boldsymbol{r}_n) = \int\frac{d^3q_1}{(2\pi)^3}\cdots\int\frac{d^3q_n}{(2\pi)^3}\; e^{i\boldsymbol{r}_1\cdot\boldsymbol{q}_1+\ldots+i\boldsymbol{r}_n\cdot\boldsymbol{q}_n}\\ \times(2\pi)^3\delta^{(3)}(\boldsymbol{q}_1+\ldots+\boldsymbol{q}_n)\\ \times\chi^{(n)}_{\mu_1\ldots\mu_n}(q_1,\ldots q_n)\,.\end{aligned} \tag{H.13}$$

Current conservation then implies the transversality of $\chi^{(n)}_{\mu_1\ldots\mu_n}$ with respect to all arguments [755],

$$q^{\mu_i}_i\chi^{(n)}_{\mu_1\ldots\mu_n}(q_1,\ldots q_n) = 0 \qquad \forall\, i=1,\ldots n\,. \tag{H.14}$$

This relation is easily established in real space. For brevity, we only consider the linear response function explicitly,

$$\begin{aligned}\partial^\mu_x\chi^{(2)}_{\mu\nu}(x,y) = &-i\langle\Psi_0|T\left[\partial^\mu\delta\hat{j}_\mu(x)\right]\delta\hat{j}_\nu(y)|\Psi_0\rangle\\ &-i\delta(x^0-y^0)\langle\Psi_0|\delta\hat{j}_0(x)\delta\hat{j}_\nu(y)-\delta\hat{j}_\nu(y)\delta\hat{j}_0(x)|\Psi_0\rangle\,.\end{aligned}$$

Now the first term on the right-hand side vanishes due to current conservation (which is also valid on the level of the operator), the second term vanishes due to the vanishing equal-time commutator,

$$\left[\hat{\psi}^\dagger(t,\boldsymbol{x})\hat{\psi}(t,\boldsymbol{x}),\hat{\psi}^\dagger(t,\boldsymbol{y})\hat{\psi}(t,\boldsymbol{y})\right] = \left[\hat{\psi}^\dagger(t,\boldsymbol{x})\hat{\psi}(t,\boldsymbol{x}),\hat{\psi}^\dagger(t,\boldsymbol{y})\alpha^k\hat{\psi}(t,\boldsymbol{y})\right] = 0\,.$$

The proof of (H.14) for higher order $\chi^{(n)}$ proceeds analogously, with the difference that all possible time orderings have to be taken into account in the second term. In the following the connected contributions of the $\chi^{(n)}$, for which all external vertices

are linked to each other in some way, will be denoted by $\chi_{\rm c}^{(n)}$, while the linear response function of the RHEG will be abbreviated by $\chi_{\mu\nu}$.

The latter function has a simple relation to the Fourier transform of the full photon propagator (H.8),

$$D_{\mu\nu}(q) = D^0_{\mu\nu}(q) + D^0_{\mu\rho}(q)\chi^{\rho\lambda}(q)D^0_{\lambda\nu}(q)\,. \tag{H.15}$$

This relation can easily be established on the basis of the equivalent of (G.5) for the photon propagator. In analogy to Eq. (G.17), one also finds a Dyson equation for the response function $\chi^{\mu\nu}$,

$$\chi^{\mu\nu}(q) = \Pi^{\mu\nu}(q) + \Pi^{\mu\rho}(q)\; D^0_{\rho\lambda}(q)\; \chi^{\lambda\nu}(q)\,. \tag{H.16}$$

Note that the present definition of the irreducible 2-point function $\Pi^{\mu\nu}$ differs from that used in Appendix G ($\omega^{\mu\nu}$) by a factor of e^2. As already indicated in the discussion of (H.8) it is more convenient for the present purpose to associate the factor of e^2 emerging from each pair of vertices in the perturbation expansion with the photon propagator than with the polarization insertion.

As a consequence of (H.14), (H.16) $\Pi^{\mu\nu}$ also satisfies the transversality relation

$$q_\mu \Pi^{\mu\nu}(q) = 0\,, \tag{H.17}$$

which determines the tensor structure of $\Pi^{\mu\nu}$. In fact, there are only two independent (4×4) polarization tensors which comply with Eq. (H.17),

$$P_{\rm L}^{\mu\nu}(q) = \frac{-1}{\boldsymbol{q}^2 q^2}\begin{pmatrix} (\boldsymbol{q}^2)^2 & \boldsymbol{q}^2 q^0 q^j \\ \boldsymbol{q}^2 q^0 q^i & (q^0)^2 q^i q^j \end{pmatrix} \tag{H.18}$$

$$P_{\rm T}^{\mu\nu}(q) = \frac{1}{\boldsymbol{q}^2}\begin{pmatrix} 0 & 0 \\ 0 & \boldsymbol{q}^2 g^{ij} + q^i q^j \end{pmatrix} \qquad (g^{ij} = -\delta_{ij}) \tag{H.19}$$

$$q_\mu P_{\rm L/T}^{\mu\nu}(q) = q_\nu P_{\rm L/T}^{\mu\nu}(q) \;=\; 0\,. \tag{H.20}$$

$\Pi^{\mu\nu}$ can therefore be written as

$$\Pi^{\mu\nu}(q) = P_{\rm L}^{\mu\nu}(q)\Pi_{\rm L}(q) - P_{\rm T}^{\mu\nu}(q)\Pi_{\rm T}(q)\,. \tag{H.21}$$

For convenience, we note some useful properties of $P_{\rm L/T}^{\mu\nu}$,

$$P_{{\rm L},\mu}{}^{\nu}(q)P_{{\rm L},\nu}{}^{\lambda}(q) = P_{{\rm L},\mu}{}^{\lambda}(q) \tag{H.22}$$

$$P_{{\rm T},\mu}{}^{\nu}(q)P_{{\rm T},\nu}{}^{\lambda}(q) = P_{{\rm T},\mu}{}^{\lambda}(q) \tag{H.23}$$

$$P_{{\rm L},\mu}{}^{\nu}(q)P_{{\rm T},\nu}{}^{\lambda}(q) = 0 \tag{H.24}$$

$$P_{{\rm L},\mu}{}^{0}(q)P_{{\rm L},0}{}^{\lambda}(q) = -\frac{\boldsymbol{q}^2}{q^2}P_{{\rm L},\mu}{}^{\lambda}(q) \tag{H.25}$$

$$P_{\rm L}^{\mu\nu}(q) + P_{\rm T}^{\mu\nu}(q) = g^{\mu\nu} - \frac{q^\mu q^\nu}{q^2} \tag{H.26}$$

$$P_{\mathrm{L},\mu}{}^{\mu}(q) = 1 \tag{H.27}$$

$$P_{\mathrm{T},\mu}{}^{\mu}(q) = 2\,. \tag{H.28}$$

If one decomposes $\Pi^{\mu\nu}$ into its vacuum (v) limit (obtained for $|\Psi_0\rangle \to |0\rangle$) and a remainder (the electron gas component—d),

$$\Pi^{\mu\nu}(q) = \Pi_{\mathrm{d}}^{\mu\nu}(q) + \Pi_{\mathrm{v}}^{\mu\nu}(q) \tag{H.29}$$

$$\Pi_{\mathrm{L}}(q) = \Pi_{\mathrm{L,d}}(q) + \Pi_{\mathrm{v}}(q) \tag{H.30}$$

$$\Pi_{\mathrm{T}}(q) = \Pi_{\mathrm{T,d}}(q) - \Pi_{\mathrm{v}}(q)\,, \tag{H.31}$$

the vacuum contribution can be recast in the tensor form (G.20), with the polarization function Π_{v} given by

$$\Pi_{\mathrm{v}}(q) = \frac{q^2}{e^2}\,\omega_{\mathrm{v}}(q)\,. \tag{H.32}$$

If one uses the polarization tensors (H.18), (H.19), the free photon propagator (G.13) and the longitudinal and transverse polarization functions $\Pi_{\mathrm{L/T}}$, the Dyson equation for $\chi^{\mu\nu}$ can be resolved as

$$\chi^{\mu\nu}(q) = \frac{\Pi_{\mathrm{L}}(q)}{1 - D^0(q)\Pi_{\mathrm{L}}(q)} P_{\mathrm{L}}^{\mu\nu}(q) - \frac{\Pi_{\mathrm{T}}(q)}{1 + D^0(q)\Pi_{\mathrm{T}}(q)} P_{\mathrm{T}}^{\mu\nu}(q)\,, \tag{H.33}$$

where, according to the modified definition (H.8), D^0 is given by (G.12) times an additional factor of e^2.

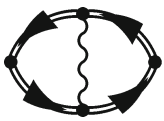
The full photon propagator $D^{\mu\nu}$ can now be obtained from Eq. (H.15) by insertion of (H.33). For a discussion of the renormalization of $D^{\mu\nu}$ it is instructive to rewrite the resulting expression in terms of the full vacuum photon propagator,

$$D_{\mathrm{v}}(q) = \frac{D^0(q)}{1 - D^0(q)\Pi_{\mathrm{v}}(q)}\,. \tag{H.34}$$

Insertion of (H.30) and (H.31) into (H.33) plus subsequent use of (H.34) allows a decoupling of the screening effects due to vacuum polarization from those originating from the actual electron gas,

$$D^{\mu\nu}(q) = \frac{D_{\mathrm{v}}(q)}{1 - D_{\mathrm{v}}(q)\Pi_{\mathrm{L,d}}(q)} P_{\mathrm{L}}^{\mu\nu}(q) + \frac{D_{\mathrm{v}}(q)}{1 + D_{\mathrm{v}}(q)\Pi_{\mathrm{T,d}}(q)} P_{\mathrm{T}}^{\mu\nu}(q)\,. \tag{H.35}$$

At first glance this form seems to suggest that $D^{\mu\nu}$ is UV-finite as soon as D_{v} is replaced by $D_{\mathrm{v,R}}$ defined by Eqs. (G.46)–(G.48). However, $\Pi_{\mathrm{L/T,d}}$ also contains UV-divergent subgraphs. The following 2-loop contribution may illustrate this point,



If one replaces G^0 by $G^0_{\rm v}+G^0_{\rm d}$ one recognizes that besides the obvious pure vacuum loop absorbed in $D_{\rm v}$ also mixtures between the first order vertex correction loop of the vacuum, Eq. (G.24), and $G^0_{\rm d}$-type propagators occur. The counterterms required to keep such subgraphs finite are, however, completely determined by vacuum QED: similar to the renormalization of overlapping divergences, each vacuum subgraph in a (larger) non-vacuum diagram has to be supplemented individually by its associated counterterm (this also holds for multi-loop vacuum subgraphs).

For the discussion of inhomogeneity corrections to the RLDA one also needs the inverse response function $\chi^{-1}_{\mu\nu}$. However, $\chi^{-1}_{\mu\nu}(q)$ can not be an inverse of $\chi_{\mu\nu}(q)$ in the conventional understanding of an inverse matrix, as the transversality relation (H.14) requires

$$q^\mu\,\chi_{\mu\nu}(q)\,\chi^{-1,\nu\rho}(q)=0\,,$$

which is not compatible with

$$\chi_{\mu\nu}(q)\chi^{-1,\nu\rho}(q)=g_\mu{}^\rho\,.$$

In the present context $\chi^{-1,\mu\nu}(q)$ is therefore defined to satisfy

$$\chi_{\mu\nu}(q)\,\chi^{-1,\nu\rho}(q)=g_\mu{}^\rho-\frac{q_\mu q^\rho}{q^2}\,. \tag{H.36}$$

When multiplied with a quantity for which the transversality condition $q_\mu f^\mu=0$ holds, $\chi^{-1,\nu\rho}$ behaves like an ordinary inverse. For this type of inverse one obtains

$$\chi^{-1,\mu\nu}(q)=-D^0(q)\,g^{\mu\nu}+\Pi^{-1,\mu\nu}(q) \tag{H.37}$$

$$\Pi^{-1,\mu\nu}(q)=\frac{1}{\Pi_{\rm L}(q)}\,P^{\mu\nu}_{\rm L}-\frac{1}{\Pi_{\rm T}(q)}\,P^{\mu\nu}_{\rm T}\,. \tag{H.38}$$

The product of (H.37) with $\chi_{\mu\nu}$, Eq. (H.33), can be shown to satisfy Eq. (H.36) by use of (H.22)–(H.24) and (H.26).

As far as explicit approximations for the polarization functions $\Pi_{\rm L/T}$ are concerned, only very little is known even in the static limit. The complete frequency dependence is available for the noninteracting limit $\Pi^{(0)}_{\rm L/T}$, i.e. the relativistic generalization of the Lindhard function [620, 756]. In addition to its vacuum part (G.23) one has

$$\begin{aligned}\Pi^{(0)}_{{\rm d},\mu\nu}(q)=&-i\int\frac{d^4p}{(2\pi)^4}{\rm tr}\left[\gamma_\mu\,G^0_{\rm d}(p)\,\gamma_\nu\,G^0_{\rm d}(p-q)\right]\\&-i\int\frac{d^4p}{(2\pi)^4}{\rm tr}\left[\gamma_\mu\,G^0_{\rm v}(p)\,\gamma_\nu\,G^0_{\rm d}(p-q)\right]\\&-i\int\frac{d^4p}{(2\pi)^4}{\rm tr}\left[\gamma_\mu\,G^0_{\rm d}(p)\,\gamma_\nu\,G^0_{\rm v}(p-q)\right]\,.\end{aligned}$$

$\Pi^{(0)}_{\mathrm{d},\mu\nu}$ is sometimes called the *no-sea* limit of the full $\Pi^{(0)}_{\mu\nu}$—quite generally the no-sea approximation $\Pi_{\mathrm{ns},\mu\nu}$ is defined by neglect of all those contributions to a closed fermion loop which do not vanish in the limit $k_\mathrm{F} \to 0$. This *no-sea* form is not identical with the result of the more frequently applied *no-pair* approximation. The latter approximation amounts to neglecting the negative energy states completely. In the present context projecting out the negative energy states at all steps of the calculation is equivalent to a complete neglect of the negative energy component $G_-(p)$ of the fermion propagator,

$$\Pi^{(0)}_{\mathrm{d},\mu\nu}(q) \neq -i \int \frac{d^4p}{(2\pi)^4} \mathrm{tr}\left[\gamma_\mu\, G^0_+(p)\, \gamma_\nu\, G^0_+(p-q)\right] = \Pi^{(0)}_{\mathrm{np},\mu\nu}(q)\,.$$

For subsequent use we note the long-wavelength expansion of the static limit of $\Pi^{(0)}_{\mu\nu}$,

$$\Pi^{(0)}_{\mathrm{L,d}}(0,\boldsymbol{q}) = -\frac{mk_\mathrm{F}\eta}{\pi^2}\left\{1 - \frac{1}{3}\left[1 + 2\frac{\beta}{\eta}\mathrm{arsinh}(\beta)\right]Q^2 + \ldots\right\} \tag{H.39}$$

$$\Pi^{(0)}_{\mathrm{T,d}}(0,\boldsymbol{q}) = \frac{mk_\mathrm{F}\eta}{\pi^2}\left\{-\frac{2}{3}\frac{\beta}{\eta}\mathrm{arsinh}(\beta)Q^2 + \ldots\right\} \tag{H.40}$$

$$\Pi^{(0)}_{\mathrm{v,R}}(0,\boldsymbol{q}) = \frac{1}{60\pi^2}\frac{\boldsymbol{q}^4}{m^2} + \ldots\,, \tag{H.41}$$

where $Q = |\boldsymbol{q}|/(2k_\mathrm{F})$ and

$$\beta = \frac{(3\pi^2 n_0)^{1/3}}{m}\,; \qquad \eta = (1+\beta^2)^{1/2}\,. \tag{H.42}$$

Beyond the noninteracting limit only the vacuum part of the 2-loop contribution to the polarization function has been evaluated [757, 758]. In addition, the screening length $\Pi_{\mathrm{L,d}}(0,\mathbf{0})$ is related to the energy density via the compressibility sum rule [759],

$$\frac{d^2}{dn_0^2}\left[t_\mathrm{s}(n_0) + e_\mathrm{xc}(n_0)\right] = -\frac{1}{\Pi_{\mathrm{L,d}}(0,\mathbf{0})}\,, \tag{H.43}$$

so that the long wavelength limit of higher orders of $\Pi_{\mathrm{L,d}}$ can be obtained from the associated contributions to the energy density. Finally, in the context of the quark-gluon gas the high temperature limits of certain classes of higher order diagrams have also been examined (see e.g. [760]). These results are, however, only of limited interest in the present context aiming at $T = 0$ and $m \geq |\boldsymbol{q}|$.

H.3 Ground State Energy

The exchange-correlation energy of the RHEG constitutes the basis for the RLDA. At the same time, it provides an instructive example for the application of the renor-

malization procedure described in Appendix G. We start by emphasizing that the ground state energy is defined with respect to the vacuum energy as in (8.56) with $V^\mu = 0$ (compare [621, 755]),

$$E^{\mathrm{RHEG}} = \langle\Psi_0|\hat{H}^{\mathrm{hom}}|\Psi_0\rangle - \langle 0|\hat{H}^{\mathrm{hom}}|0\rangle + \Delta E^{\mathrm{hom}}\,, \tag{H.44}$$

where $\langle 0|\hat{H}^{\mathrm{hom}}|0\rangle$ is the energy of the interacting, homogeneous vacuum and ΔE^{hom} represents the counterterms required to keep E^{RHEG} UV-finite. In the case of the electron gas Eq. (H.44) is applied on the level of the energy density, rather than the infinite energy itself.

The kinetic energy density t_{s} of the noninteracting RHEG can be evaluated without application of the UV-renormalization procedure [761],

$$\begin{aligned} t_{\mathrm{s}}(n_0) &= \langle\Psi_0|\Big[\hat{\bar{\psi}}(x), \Big(-i\boldsymbol{\gamma}\cdot\boldsymbol{\nabla} + (1-\gamma^0)m\Big)\hat{\psi}(x)\Big]|\Psi_0\rangle \\ &\quad -\langle 0|\Big[\hat{\bar{\psi}}(x), \Big(-i\boldsymbol{\gamma}\cdot\boldsymbol{\nabla} + (1-\gamma^0)m\Big)\hat{\psi}(x)\Big]|0\rangle \\ &= i\lim_{y\to x}{}_{\mathrm{s}}\ \mathrm{tr}\Big[\Big(-i\boldsymbol{\gamma}\cdot\boldsymbol{\nabla} + (1-\gamma^0)m\Big)G_{\mathrm{d}}^0(x-y)\Big] \\ &= \frac{k_{\mathrm{F}}^5}{10\pi^2 m}\,\Phi_{\mathrm{s}}(\beta) \end{aligned} \tag{H.45}$$

$$\Phi_{\mathrm{s}}(\beta) = \frac{10}{\beta^5}\left[\frac{1}{8}\Big(\beta\eta^3 + \beta^3\eta - \mathrm{arsinh}(\beta)\Big) - \frac{1}{3}\beta^3\right] \tag{H.46}$$

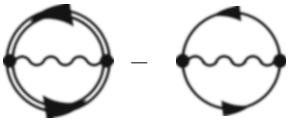
(the electron rest mass has been subtracted). The Hartree (electrostatic) energy of the RHEG vanishes, if one takes the neutralizing positive charge background into account. Following closely the derivation of Eq. (4.88), the xc-energy of the RHEG can be written in terms of a coupling constant integral over the current–current response function [618, 538],

$$e_{\mathrm{xc}}(n_0) = \frac{i}{2}\int_0^1 d\lambda \int \frac{d^4q}{(2\pi)^4}\, D^0_{\mu\nu}(q)\Big[\chi_\lambda^{\mu\nu}(q) - \chi_{\mathrm{v},\lambda}^{\mu\nu}(q)\Big] + \Delta e^{\mathrm{hom}}\,. \tag{H.47}$$

$\chi_\lambda^{\mu\nu}$ is given by (H.33) with the coupling strength e^2 replaced by λe^2, $\chi_{\mathrm{v},\lambda}^{\mu\nu}$ represents its vacuum limit and Δe^{hom} is the energy density corresponding to the counterterm ΔE^{hom}.

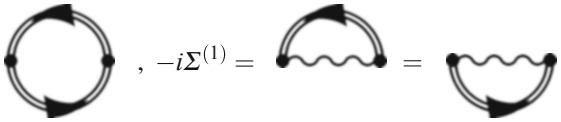
The first order term (in e^2) in (H.47), i.e. the exchange energy of the RHEG (according to Eq. (8.92)), is the simplest energy contribution for which the UV-renormalization is nontrivial. The basic problem associated with the renormalization of energies (rather than Green's functions) is that energy expressions can not be rewritten entirely in terms of renormalized n-point functions. At least one overall loop integration remains to be treated separately (the q-integration in (H.47)). As an additional complication, this outermost loop integration often leads to overlapping divergences. An example for this statement is provided by the exchange energy, which is obtained if the full $\chi_\lambda^{\mu\nu}$ in Eq. (H.47) is replaced by its noninteracting limit $\Pi^{(0),\mu\nu}$. Visualizing the resulting integral graphically,

$$-2ie_{\rm x}(n_0) = \quad - \quad , \tag{H.48}$$



one realizes that three divergent 1-loop subgraphs contribute to the electron gas loop,

$$-i\Pi^{(0)}_{\mu\nu} = \quad , \quad -i\Sigma^{(1)} = \quad = \quad . \tag{H.49}$$



While the UV-divergence of the $\Pi^{(0)}_{\mu\nu}$-subgraph is eliminated by the subtraction of the vacuum exchange energy in (H.48), the two (identical) self-energy subgraphs require additional counterterms. As one is facing overlapping divergences in (H.48) each divergent subgraph has to be renormalized individually. Of course, only the vacuum contribution to $\Sigma^{(1)}$ requires renormalization,

$$\begin{aligned} e_{\rm x}(n_0) = \frac{i}{2}\int \frac{d^4q}{(2\pi)^4}\, D^0_{\mu\nu}(q)\, \Big[\Pi^{(0),\mu\nu}(q) - \Pi^{(0),\mu\nu}_{\rm v}(q)\Big] \\ -i\int \frac{d^4p}{(2\pi)^4}\, {\rm tr}\Big[G^0_{\rm d}(p)\Delta\Sigma^{(1)}_{\rm v}(p)\Big]\,. \end{aligned} \tag{H.50}$$

The second line represents the lowest order contribution to the UV-counterterm $\Delta e^{\rm hom}$. As discussed in detail in Appendix G, the self-energy counterterm $\Delta\Sigma^{(1)}_{\rm v}$ is defined so that the renormalized vacuum self-energy $\Sigma_{\rm v,R}$, Eq. (G.44), satisfies the standard on-shell normalization condition (G.45), i.e. on the 1-loop level one obtains (G.58). Using the decomposition of G^0, Eq. (H.2), $e_{\rm x}(n_0)$ can thus be rewritten as

$$\begin{aligned} e_{\rm x}(n_0) = \frac{1}{2}\int \frac{d^4q}{(2\pi)^4}\int \frac{d^4p}{(2\pi)^4}\, D^0_{\mu\nu}(q)\, {\rm tr}\left[G^0_{\rm d}(p+q)\gamma^\mu G^0_{\rm d}(p)\gamma^\nu\right] \\ -i\int \frac{d^4p}{(2\pi)^4}\, {\rm tr}\Big[G^0_{\rm d}(p)\Sigma^{(1)}_{\rm v,R}(p)\Big]\,. \end{aligned} \tag{H.51}$$

The second term on the right-hand side vanishes according to Eqs. (H.3), (G.45),

$$\Big[(\not{p}+m)\Sigma_{\rm v,R}(p)\Big]_{p^2=m^2} = 0\,.$$

Consequently, the standard renormalization scheme eliminates the vacuum corrections to $e_{\rm x}(n_0)$ completely. The first line of (H.51) can be evaluated straightforwardly [618–620],

$$e_{\rm x}(n_0) = e^{\rm NRHEG}_{\rm x}(n_0)\; \Phi_{\rm x}(\beta) \tag{H.52}$$

$$e_{\mathrm{x}}^{\mathrm{NRHEG}}(n_0) = -\frac{e^2}{4\pi^3}\, k_{\mathrm{F}}^4 \tag{H.53}$$

$$\Phi_{\mathrm{x}}(\beta) = 1 - \frac{3}{2}\left[\frac{\eta}{\beta} - \frac{1}{\beta^2}\mathrm{arsinh}(\beta)\right]^2. \tag{H.54}$$

Moreover, using the decomposition of the photon propagator into the Coulomb and the transverse interaction, $e_{\mathrm{x}}(n_0)$ can be split accordingly [535, 620],

$$e_{\mathrm{x}}^{\mathrm{C/T}}(n_0) = e_{\mathrm{x}}^{\mathrm{NRHEG}}(n_0)\, \Phi_{\mathrm{x}}^{\mathrm{C/T}}(\beta) \tag{H.55}$$

$$\begin{aligned}\Phi_{\mathrm{x}}^{\mathrm{C}}(\beta) = {} & \frac{5}{6} + \frac{1}{3\beta^2} + \frac{2\eta}{3\beta}\mathrm{arsinh}(\beta) \\ & - \frac{2\eta^4}{3\beta^4}\ln(\eta) - \frac{1}{2}\left(\frac{\eta}{\beta} - \frac{\mathrm{arsinh}(\beta)}{\beta^2}\right)^2\end{aligned} \tag{H.56}$$

$$\begin{aligned}\Phi_{\mathrm{x}}^{\mathrm{T}}(\beta) = {} & \frac{1}{6} - \frac{1}{3\beta^2} - \frac{2\eta}{3\beta}\mathrm{arsinh}(\beta) \\ & + \frac{2\eta^4}{3\beta^4}\ln(\eta) - \left(\frac{\eta}{\beta} - \frac{\mathrm{arsinh}(\beta)}{\beta^2}\right)^2.\end{aligned} \tag{H.57}$$

The UV-renormalization procedure is particularly involved for the correlation energy e_{c}, which we also discuss here for completeness. Most of the counterterms provided by Δe^{hom} are, however, included if the basic expression (H.47) is rewritten in terms of the renormalized response function $\chi_{\mathrm{R},\lambda}^{\mu\nu}$,

$$e_{\mathrm{xc}}(n_0) = \frac{i}{2}\int_0^1 d\lambda \int \frac{d^4q}{(2\pi)^4}\, D_{\mu\nu}^0(q)\left[\chi_{\mathrm{R},\lambda}^{\mu\nu}(q) - \chi_{\mathrm{v,R},\lambda}^{\mu\nu}(q)\right] + \Delta\tilde{e}^{\mathrm{hom}} \tag{H.58}$$

(the exchange energy has not been subtracted). The only remaining divergence (to be eliminated by $\Delta\tilde{e}^{\mathrm{hom}}$) now originates from the outermost loop integration in (H.58). It can be explicitly discussed within the so-called random phase (or ring) approximation (RPA) in which $\Pi_{\mathrm{L/T}}$ is approximated by its 1-loop contribution $\Pi_{\mathrm{L/T}}^{(0)}$ [618, 762]. Insertion of Eq. (H.33) into (H.58) then gives

$$\begin{aligned}e_{\mathrm{xc}}^{\mathrm{RPA}}(n_0) = \frac{i}{2}\int_0^1 d\lambda \int \frac{d^4q}{(2\pi)^4}\Bigg[& \frac{D^0(q)\Pi_{\mathrm{L}}^{(0)}(q)}{1-\lambda D^0(q)\Pi_{\mathrm{L}}^{(0)}(q)} - 2\frac{D^0(q)\Pi_{\mathrm{T}}^{(0)}(q)}{1+\lambda D^0(q)\Pi_{\mathrm{T}}^{(0)}(q)} \\ & - 3\frac{D^0(q)\Pi_{\mathrm{v,R}}^{(0)}(q)}{1-\lambda D^0(q)\Pi_{\mathrm{v,R}}^{(0)}(q)}\Bigg] + \Delta\tilde{e}^{\mathrm{hom,RPA}}.\end{aligned}$$

The coupling constant integration can be performed directly, if Eqs. (H.30), (H.31) and (H.34) are used,

$$e_{\rm xc}^{\rm RPA}(n_0) = -\frac{i}{2}\int \frac{d^4q}{(2\pi)^4}\left[\ln\left[1-D_{\rm v,R}(q)\Pi_{\rm L,d}^{(0)}(q)\right] + 2\ln\left[1+D_{\rm v,R}(q)\Pi_{\rm T,d}^{(0)}(q)\right]\right] + \Delta\tilde{e}^{\rm hom,RPA}. \quad \text{(H.59)}$$

At this point it is convenient to define the vacuum-screened exchange energy,

$$e_{\rm x,s}(n_0) = \frac{i}{2}\int \frac{d^4q}{(2\pi)^4}\left[D_{\rm v,R}(q)\Pi_{\rm L,d}^{(0)}(q) - 2D_{\rm v,R}(q)\Pi_{\rm T,d}^{(0)}(q)\right] + \Delta\tilde{e}^{\rm hom,RPA}, \quad \text{(H.60)}$$

which requires renormalization similar to its unscreened counterpart. After subtraction of $e_{\rm x,s}$ from $e_{\rm xc}^{\rm RPA}$ one obtains for the correlation energy [762]

$$e_{\rm c,s}^{\rm RPA}(n_0) = -\frac{i}{2}\int \frac{d^4q}{(2\pi)^4}\left[\ln\left[1-D_{\rm v,R}(q)\Pi_{\rm L,d}^{(0)}(q)\right] + 2\ln\left[1+D_{\rm v,R}(q)\Pi_{\rm T,d}^{(0)}(q)\right] + D_{\rm v,R}(q)\Pi_{\rm L,d}^{(0)}(q) - 2D_{\rm v,R}(q)\Pi_{\rm T,d}^{(0)}(q)\right]. \quad \text{(H.61)}$$

This expression is UV-convergent as it stands, as the lowest order diagram included in (H.61) contains $\Pi_{\rm L/T,d}^{(0)}$ already two times.[1] Finally, one can define the *no-sea* approximation of (H.61) by neglecting all screening effects due to vacuum polarization. Decomposing the result into a Coulomb and a transverse component, one ends up with

$$e_{\rm c,ns}^{\rm C,RPA}(n_0) = -\frac{i}{2}\int \frac{d^4q}{(2\pi)^4}\left\{\ln\left|1-D^0(q)\Pi_{\rm L,d}^{(0)}(q)\right| + D^0(q)\Pi_{\rm L,d}^{(0)}(q)\right\} \quad \text{(H.62)}$$

$$e_{\rm c,ns}^{\rm T,RPA}(n_0) = -i\int \frac{d^4q}{(2\pi)^4}\left\{\ln\left|1+D^0(q)\Pi_{\rm T,d}^{(0)}(q)\right| - D^0(q)\Pi_{\rm T,d}^{(0)}(q)\right\}. \quad \text{(H.63)}$$

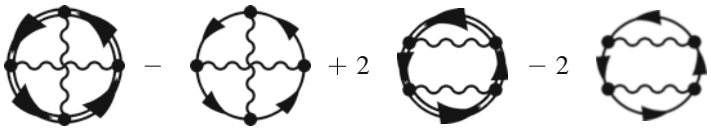
$e_{\rm c,ns}^{\rm C/T,RPA}(n_0)$ has been evaluated numerically for arbitrary n_0 [538, 622]. The high-density (ultrarelativistic) limit of $e_{\rm c,ns}^{\rm RPA}$ is given by [618, 621]

$$e_{\rm c,ns}^{\rm RPA}(n_0) \xrightarrow[\beta\gg 1]{} \frac{e^4k_{\rm F}^4}{12\pi^4}\left(\frac{3}{2}\ln\frac{\alpha}{\pi} + 1.3761 + \ldots\right) = \frac{e^4k_{\rm F}^4}{12\pi^4}\left(-7.796 + \ldots\right), \quad \text{(H.64)}$$

where α is the fine structure constant.

In order to arrive at the RPA+, which we understand as the combination of the RPA with the remaining second order (e^4) contributions, the two second order exchange (SOX) diagrams,

[1] After Wick-rotation of q_0 in (H.61) one e.g. finds $\Pi_{\rm L,d}^{(0)}(iq_0,\boldsymbol{q}) \sim (\boldsymbol{q}^2+q_0^2)^{-1}$ and $\Pi_{\rm v,R}^{(0)}(iq^0,\boldsymbol{q}) \sim (\boldsymbol{q}^2+q_0^2)\ln|\boldsymbol{q}^2+q_0^2|$ for large q^0 and $|\boldsymbol{q}|$ so that two factors of $\Pi_{\rm L,d}^{(0)}(iq^0,\boldsymbol{q})$ together with the two photon propagators are sufficient to ensure UV-convergence of the outermost loop integral.



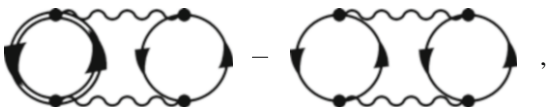
, (H.65)

have to be added to $e_{\mathrm{c}}^{\mathrm{RPA}}$. In contrast to the nonrelativistic situation the two rightmost diagrams do not vanish. Both types of diagrams require renormalization beyond the subtraction of their vacuum limit indicated in Eq. (H.65). The density dependence of these diagrams is not known completely. In the ultrarelativistic limit one finds for the sum of both graphs (the individual contributions are not gauge invariant) [621]

$$e_{\mathrm{c}}^{\mathrm{SOX}}(n_0) \xrightarrow[\beta\gg 1]{} \frac{e^4 k_{\mathrm{F}}^4}{12\pi^4}\left(-3.18 \pm 0.12\right), \tag{H.66}$$

so that $e_{\mathrm{c}}^{\mathrm{SOX}}$ amounts to roughly 40% of the RPA in this limit.

One can also analyze the 2-loop contribution to the screened exchange (H.60),



which (in our definition) is beyond the *no-sea* approximation. Its ultrarelativistic limit is [621],

$$e_{\mathrm{x,s}}^{(2)}(n_0) \xrightarrow[\beta\gg 1]{} \frac{e^4 k_{\mathrm{F}}^4}{12\pi^4}\left[\ln\left(2\frac{k_{\mathrm{F}}}{m}\right) - \frac{11}{6}\right]. \tag{H.67}$$

In the limit of very high densities $e_{\mathrm{x,s}}^{(2)}$ thus dominates over all other known xc-energy contributions. However, the densities required for $e_{\mathrm{x,s}}^{(2)}$ to be of the same order of magnitude as $e_{\mathrm{c}}^{\mathrm{RPA}+}$ are extremely high, $k_{\mathrm{F}}/m \approx 10^3$, so that $e_{\mathrm{x,s}}^{(2)}$ is not relevant for electronic structure calculations.

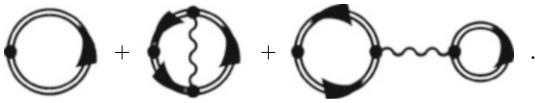
No calculations of e_{c} beyond the RPA+ are found in the literature.

H.4 Ground State Four Current

After the extensive discussion of the ground state energy little remains to be said concerning the ground state four current of the RHEG. Due to norm conservation, the interacting current must be identical with the current of the noninteracting RHEG, that is $n_0\, g^{\mu 0}$, in real space. If one expresses the current expectation value in terms of the interacting propagator (H.1),

$$\langle \Psi_0 | \hat{j}_\mu(x) | \Psi_0 \rangle = -\, i \lim_{y\to x}{}_{\mathrm{s}}\, \mathrm{tr}\left[G(x,y)\gamma_\mu\right],$$

one realizes that all higher order contributions resulting from the perturbation expansion of G must cancel order by order. This will be demonstrated explicitly for all first order vacuum contributions. To first order one obtains diagrammatically

$ie\langle\Psi_0|\hat{j}_\mu(x)|\Psi_0\rangle =$  .

One first observes that in the pure vacuum limit, $G^0 \to G^0_{\rm v}$, all loops vanish, as at least one part of the graph is a fermion loop with an odd number of vertices (Furry's theorem)—only mixtures of vacuum subgraphs with non-vacuum components can contribute to j^μ. Moreover, the right-hand first order diagram need not be considered any further, as in addition to the electronic charge density the neutralizing positive background charge density has to be coupled to the polarization graph. Consequently, all diagrams containing tadpoles do not contribute. One is thus left with the vacuum subgraphs in the remaining first order diagram. Two vacuum subgraphs are identified, the vertex correction (left part) and the self-energy (right part). However, after renormalization the vertex correction vanishes on the mass shell due to the normalization condition (G.52). Therefore the combination of this vacuum subgraph with the remainder of the diagram, i.e. the product $\Gamma_{\rm v,R} G^0_{\rm d}$, is zero. Similarly, the vacuum self-energy is proportional to $(\not{p} - m)^2$ on the mass shell, Eq. (G.45), so that products as $G^0_{\rm d}\Sigma_{\rm v,R}G^0_{\rm v}$ vanish. Consequently, after renormalization the terms containing vacuum subgraphs give no contribution to the four current, as required. It is obvious that the argument given also applies to higher order contributions. The necessary counterterms will be denoted as $\Delta j^{\rm hom}_\mu$,

$$j_\mu = \langle\Psi_0|\hat{j}_\mu(x)|\Psi_0\rangle + \Delta j^{\rm hom}_\mu = n_0\, g_{\mu 0}\,. \tag{H.68}$$

As in the case of $\Delta e^{\rm hom}$, $\Delta j^{\rm hom}_\mu$ is determined by the renormalization of all relevant vacuum subgraphs.

Appendix I
Renormalization of Inhomogeneous Electron Gas

In order to prepare the discussion of the relativistic generalization of the HK-theorem in Sect. 8.3 we finally consider the renormalization procedure for inhomogeneous systems, i.e. the full Lagrangian (8.11). Since the underlying renormalization program of vacuum QED is formulated within a perturbative framework (see Appendix G), we assume that the perturbing potential V^μ is sufficiently weak to allow a power series expansion of all relevant quantities with respect to V^μ. Within this approach one can explicitly derive the counterterms required for the field theoretical version of the relativistic KS equations, i.e. for the four current and kinetic energy of noninteracting particles. In this Appendix again $\hbar = c = 1$ is used.

The first quantity of interest is the four current $\delta j^\mu(\boldsymbol{r})$ induced by $V^\mu(\boldsymbol{r})$. The perturbation expansion of δj^μ with respect to V^μ can be written as

$$\delta j_\mu(\boldsymbol{r}) = \sum_{n=1}^{\infty} \frac{(-e)^n}{n!} \int d^3 r_1 \ldots \int d^3 r_n \, \chi^{(n+1)}_{\mathrm{c},\mu\mu_1\ldots\mu_n}(\boldsymbol{r}, \boldsymbol{r}_1, \ldots \boldsymbol{r}_n) \times V^{\mu_1}(\boldsymbol{r}_1) \ldots V^{\mu_n}(\boldsymbol{r}_n) \; + \; \Delta j_\mu^{\mathrm{inhom}}(\boldsymbol{r}) \,, \tag{I.1}$$

where $\chi^{(n)}_{\mathrm{c},\mu_1\ldots\mu_n}$ represents the static, connected response functions of the RHEG (for their precise definition see Appendix H) and $\Delta j_\mu^{\mathrm{inhom}}$ denotes the counterterms which keep δj_μ UV-finite. Of course, δj^μ satisfies current conservation,

$$\partial_\mu \delta j^\mu(\boldsymbol{r}) = \boldsymbol{\nabla} \cdot \delta \boldsymbol{j}(\boldsymbol{r}) = 0 \,, \qquad \int d^3 r \, \delta j^0(\boldsymbol{r}) = 0 \,, \tag{I.2}$$

which is directly related to the transversality of $\chi^{(n)}_{\mathrm{c},\mu_1\ldots\mu_n}$ displayed in Eq. (H.14).

The induced current (I.1) is automatically UV-finite if the expansion is based on renormalized response functions, i.e. $\Delta j_\mu^{\mathrm{inhom}}$ just sums up the terms required for the transition from the unrenormalized $\chi^{(n)}_{\mathrm{c},\mu_1\ldots\mu_n}$ to their renormalized counterparts. Introducing an expansion of $\Delta j_\mu^{\mathrm{inhom}}$ in powers of V^μ one thus has

$$\Delta j_\mu^{\text{inhom}} = \sum_{n=1}^{\infty} \frac{(-e)^n}{n!} \int d^3 r_1 \ldots \int d^3 r_n \, \Delta\chi^{(n+1)}_{\mu\mu_1\ldots\mu_n}(\boldsymbol{r}, \boldsymbol{r}_1, \ldots \boldsymbol{r}_n) \times V^{\mu_1}(\boldsymbol{r}_1) \ldots V^{\mu_n}(\boldsymbol{r}_n) \,, \tag{I.3}$$

where $\Delta\chi^{(n)}_{\mu_1\ldots\mu_n}$ represents the counterterms which keep the connected response function $\chi^{(n)}_{\text{c},\mu_1\ldots\mu_n}$ of the RHEG finite.

It is instructive to analyze $\Delta j_\mu^{\text{inhom}}$ for the noninteracting limit of (I.1). Using the notation of Eqs. (F.39), (F.40) and (H.7) and taking into account the fermion sign rule, the induced current is given graphically by

$ie\delta j_\mu^{(0)} =$  (I.4)

(the multiplicities resulting from different ordering of vertices in case of the higher order response functions with $n \geq 2$ compensate the prefactor $1/n!$ in (I.1)). While the noninteracting 3-point function, i.e. the second graph, is UV-finite due to Furry's theorem, the noninteracting 4-point function (third diagram) is UV-finite due to its transversality and all higher order response functions are overall convergent. The only divergent term to be examined is contained in the first diagram. The counterterm for the vacuum component of $\chi^{(0)}_{\mu\nu}$, $\chi^{(0)}_{\text{v},\mu\nu} = \Pi^{(0)}_{\text{v},\mu\nu} = \omega^{(0)}_{\text{v},\mu\nu}/e^2$, has been derived in Appendix G. Using dimensional regularization, one obtains Eq. (G.60) as counterterm to the lowest order 2-point function and thus after Fourier transformation,

$$\Delta j_\mu^{(0)}(\boldsymbol{r}) = \frac{e}{12\pi^2} \Gamma\left(\frac{4-d}{2}\right) \boldsymbol{\nabla}^2 V_\mu(\boldsymbol{r}) \,, \tag{I.5}$$

if Coulomb gauge, $\boldsymbol{\nabla} \cdot \boldsymbol{V}(\boldsymbol{r}) = 0$, is used.

The second quantity of interest is the energy shift resulting from the perturbing potential. This shift can be evaluated by use of the coupling constant integration technique with respect to V^μ. If one scales the associated Hamiltonian (8.43) by λ,

$$\hat{H}_{\text{ext}}(\lambda) = -\lambda e \int d^3 r \, \hat{j}^\mu(\boldsymbol{r}) V_\mu(\boldsymbol{r}) \,, \tag{I.6}$$

one obtains for the corresponding renormalized ground state energy

$$\begin{aligned} E(\lambda) = {} & \langle \Psi_0(\lambda) | \hat{H}^{\text{hom}} + \hat{H}_{\text{ext}}(\lambda) | \Psi_0(\lambda) \rangle \\ & - \langle 0 | \hat{H}^{\text{hom}} | 0 \rangle + \Delta E^{\text{hom}} + \Delta E^{\text{inhom}}(\lambda) \,. \end{aligned} \tag{I.7}$$

Here $|\Psi_0(\lambda)\rangle$ denotes the ground state of the scaled Hamiltonian $\hat{H}^{\text{hom}} + \hat{H}_{\text{ext}}(\lambda)$. ΔE^{hom} provides the counterterms which, together with the vacuum expectation value $\langle 0 | \hat{H}^{\text{hom}} | 0 \rangle$, keep $E(\lambda)$ finite for $\lambda = 0$. $\Delta E^{\text{inhom}}(\lambda)$ contains all remaining counterterms. The energy of actual interest, corresponding to $\lambda = 1$, can be obtained by coupling constant integration, following the scheme in Sect. 4.2.1. Using proper normalization for all λ,

$$\langle\Psi_0(\lambda)|\Psi_0(\lambda)\rangle = 1\,,$$

one obtains by differentiation of (I.7) with respect to λ and subsequent integration from 0 to 1,

$$E(\lambda=1) = E^{\mathrm{RHEG}} - e\int_0^1 d\lambda \int d^3r\; j^\mu(\lambda,\boldsymbol{r})\, V_\mu(\boldsymbol{r}) + \Delta E^{\mathrm{inhom}}(\lambda=1)\,.$$

In this expression $j^\mu(\lambda,\boldsymbol{r})$ stands for the ground state current resulting for the coupling strength λ,

$$j^\mu(\lambda,\boldsymbol{r}) = \langle\Psi_0(\lambda)|\hat{j}^\mu(\boldsymbol{r})|\Psi_0(\lambda)\rangle\,,$$

and $E^{\mathrm{RHEG}} = E(\lambda=0)$ is to be understood as renormalized (ΔE^{hom} has been absorbed into E^{RHEG}). Insertion of (I.1) then allows to perform the λ-integration,

$$\begin{aligned} E = E^{\mathrm{RHEG}} &- e\int d^3r\,\langle\Psi_0(\lambda=0)|\hat{j}^\mu(\boldsymbol{r})|\Psi_0(\lambda=0)\rangle\, V_\mu(\boldsymbol{r}) \\ &+ \sum_{n=2}^{\infty}\frac{(-e)^n}{n!}\int d^3r_1\ldots\int d^3r_n\,\chi^{(n)}_{\mathrm{c},\mu_1\ldots\mu_n}(\boldsymbol{r}_1,\ldots\boldsymbol{r}_n) \\ &\qquad\qquad \times V^{\mu_1}(\boldsymbol{r}_1)\ldots V^{\mu_n}(\boldsymbol{r}_n) \\ &+\Delta E^{\mathrm{inhom}}\,. \end{aligned} \tag{I.8}$$

At this point one can examine $\Delta E^{\mathrm{inhom}}$ in more detail. Its component linear in V^μ,

$$\Delta E^{\mathrm{inhom}} = -e\int d^3r\,\Delta E^{(1)}_\mu V^\mu(\boldsymbol{r}) + \mathscr{O}(V^2)\,,$$

has to keep the current expectation value of the unperturbed system, i.e. of the interacting RHEG, finite,

$$\langle\Psi_0(0)|\hat{j}_\mu(\boldsymbol{r})|\Psi_0(0)\rangle + \Delta E^{(1)}_\mu = n_0\, g_{\mu 0}\,. \tag{I.9}$$

It agrees with $\Delta j^{\mathrm{hom}}_\mu$ defined via Eq. (H.68). As discussed in Appendix F, $\Delta j^{\mathrm{hom}}_\mu$ vanishes in the noninteracting limit. All higher order ingredients of $\Delta E^{\mathrm{inhom}}$ are determined by the renormalization of the $\chi^{(n)}_{\mathrm{c},\mu_1\ldots\mu_n}$. The counterterm $\Delta E^{\mathrm{inhom}}$ is therefore closely related to $\Delta j^{\mathrm{inhom}}_\mu$, Eq. (I.3),

$$\begin{aligned} \Delta E^{\mathrm{inhom}} = \sum_{n=1}^{\infty}\frac{(-e)^n}{n!}\int d^3r_1\ldots\int d^3r_n\,\Delta\chi^{(n)}_{\mu_1\ldots\mu_n}(\boldsymbol{r}_1,\ldots\boldsymbol{r}_n) \\ \times V^{\mu_1}(\boldsymbol{r}_1)\ldots V^{\mu_n}(\boldsymbol{r}_n)\,, \end{aligned} \tag{I.10}$$

where $\Delta\chi^{(1)}_\mu \equiv \Delta j^{\mathrm{hom}}_\mu$ has been introduced for brevity. The only counterterm on the noninteracting level, corresponding to (I.5), is given by

$$\Delta E^{(0),\mathrm{inhom}} = -\frac{e^2}{24\pi^2}\Gamma\left(\frac{4-d}{2}\right)\int d^3r\, V_\mu(\boldsymbol{r})\boldsymbol{\nabla}^2 V^\mu(\boldsymbol{r})\,. \tag{I.11}$$

The total energy counterterm (I.10) can be decomposed into contributions to the individual energy components. Again this can be demonstrated directly for the non-interacting case. Here the total energy is just a sum of the external potential energy,

$$E_{\rm ext} = -e \int d^3r V_\mu(\boldsymbol{r}) \left[g^{\mu 0} n_0 + \delta j^\mu(\boldsymbol{r}) \right] + \Delta E_{\rm ext}^{(0),{\rm inhom}}, \tag{I.12}$$

which, consistent with (I.5), requires the counterterm

$$\Delta E_{\rm ext}^{(0),{\rm inhom}} = -\frac{e^2}{12\pi^2} \Gamma\left(\frac{4-d}{2}\right) \int d^3r V_\mu(\boldsymbol{r}) \boldsymbol{\nabla}^2 V^\mu(\boldsymbol{r}), \tag{I.13}$$

and the noninteracting kinetic contribution $T_{\rm s}$ which absorbs the remainder of (I.11),

$$\Delta T_{\rm s}^{\rm inhom} = \frac{e^2}{24\pi^2} \Gamma\left(\frac{4-d}{2}\right) \int d^3r V_\mu(\boldsymbol{r}) \boldsymbol{\nabla}^2 V^\mu(\boldsymbol{r}). \tag{I.14}$$

The first order counterterms (I.5) and (I.11) are an explicit manifestation of the fact that, quite generally, Δj^μ and $\Delta E^{\rm inhom}$ are completely determined by the external potential and the average density n_0 of the weakly inhomogeneous system. Only these two quantities enter Eqs. (I.3) and (I.10). The resulting dependence of Δj^μ and $\Delta E^{\rm inhom}$ on V^μ is obvious, while that on n_0 results from the multi-loop contributions to the response functions.

Appendix J
Gradient Corrections to the Relativistic LDA

While the RLDA for $E_{\rm xc}[j]$ is based on the xc-energy density of the RHEG, Eq. (H.47), the expansions (I.1) and (I.8) allow the derivation of systematic corrections to the RLDA. Restricting the discussion to the linear response contributions, Eq. (I.1) reduces to

$$\delta j^{\mu}(\boldsymbol{q}) = -e\chi^{\mu\nu}(q^0 = 0, \boldsymbol{q}) V_{\nu}(\boldsymbol{q}), \tag{J.1}$$

with the total current given by $j^{\mu}(\boldsymbol{x}) = n_0 g^{\mu 0} + \delta j^{\mu}(\boldsymbol{x})$ (response functions are always understood to be renormalized in this appendix, so that counterterms are not displayed explicitly; $\hbar = c = 1$ is again used). Using the inverse of $\chi^{\mu\nu}$, Eq. (H.36), one can rewrite (J.1) as

$$\chi^{-1}_{\rho\mu}(0, \boldsymbol{q}) \delta j^{\mu}(\boldsymbol{q}) = -eV_{\rho}(\boldsymbol{q}), \tag{J.2}$$

where Coulomb gauge has been utilized. With Eqs. (J.1) and (J.2) the second order (V^2) contribution to (I.8) can be rewritten as

$$\delta E^{\rm LR} = -e \int \frac{d^3q}{(2\pi)^3} \delta j^{\mu}(\boldsymbol{q}) V_{\mu}(\boldsymbol{q}) - \frac{1}{2} \int \frac{d^3q}{(2\pi)^3} \delta j^{\mu}(\boldsymbol{q}) \chi^{-1}_{\mu\nu}(0, \boldsymbol{q}) \delta j^{\nu}(-\boldsymbol{q}).$$

After insertion of the result (H.37) for the inverse response function,

$$\begin{aligned} \delta E^{\rm LR} = &-e \int \frac{d^3q}{(2\pi)^3} \delta j^{\mu}(\boldsymbol{q}) V_{\mu}(\boldsymbol{q}) + \frac{1}{2} \int \frac{d^3q}{(2\pi)^3} \delta j^{\mu}(\boldsymbol{q}) D^0(-\boldsymbol{q}^2) \delta j_{\mu}(-\boldsymbol{q}) \\ &- \frac{1}{2} \int \frac{d^3q}{(2\pi)^3} \delta j^{\mu}(\boldsymbol{q}) \Pi^{-1}_{\mu\nu}(0, \boldsymbol{q}) \delta j^{\nu}(-\boldsymbol{q}), \end{aligned} \tag{J.3}$$

one can identify the first term as the linear response contribution to $E_{\rm ext}$, Eq. (8.82), the second one as the induced Hartree energy (8.84). The third term represents the inhomogeneity corrections to the kinetic energy ($\delta T_{\rm s}^{\rm LR}$) and to the xc-energy ($\delta E_{\rm xc}^{\rm LR}$). $\delta T_{\rm s}^{\rm LR}$ is obtained from the noninteracting limit of $\Pi^{-1}_{\mu\nu}(\boldsymbol{q}, 0)$, so that the two contributions can be separated easily. Utilizing the tensor structure of $\Pi^{-1}_{\mu\nu}(\boldsymbol{q}, 0)$,

Eq. (H.38), as well as current conservation, $\boldsymbol{q}\cdot\boldsymbol{j}(\boldsymbol{q})=0$, one arrives at

$$\delta T_{\rm s}^{\rm LR}+\delta E_{\rm xc}^{\rm LR}=-\frac{1}{2}\int\frac{d^3q}{(2\pi)^3}\left\{\frac{\delta j^0(\boldsymbol{q})\,\delta j^0(-\boldsymbol{q})}{\Pi_{\rm L}(0,\boldsymbol{q})}+\frac{\boldsymbol{j}(\boldsymbol{q})\cdot\boldsymbol{j}(-\boldsymbol{q})}{\Pi_{\rm T}(0,\boldsymbol{q})}\right\}, \tag{J.4}$$

where $\delta\boldsymbol{j}(\boldsymbol{q})=\boldsymbol{j}(\boldsymbol{q})$ has been used.

In the next step one extracts that component of (J.4) which is part of the RLDA. This procedure involves only the δj^0-dependent term in (J.4) and follows closely the discussion of Sect. 4.4.1. For the weakly inhomogeneous gas of interest an expansion of the RLDA energy to the order $(\delta j^0)^2$ gives

$$\begin{aligned}
&T_{\rm s}^{\rm RLDA}[n_0+\delta j^0]+E_{\rm xc}^{\rm RLDA}[n_0+\delta j^0]\\
&=\int d^3r\,\left[t_{\rm s}(n_0+\delta j^0(\boldsymbol{r}))+e_{\rm xc}(n_0+\delta j^0(\boldsymbol{r}))\right]\\
&=\int d^3r\left[t_{\rm s}(n_0)+e_{\rm xc}(n_0)+\left(\frac{dt_{\rm s}}{dn_0}(n_0)+\frac{de_{\rm xc}}{dn_0}(n_0)\right)\delta j^0(\boldsymbol{r})\right.\\
&\qquad\left.+\frac{1}{2}\left(\frac{d^2t_{\rm s}}{dn_0^2}(n_0)+\frac{d^2e_{\rm xc}}{dn_0^2}(n_0)\right)\delta j^0(\boldsymbol{r})^2+\ldots\right].
\end{aligned} \tag{J.5}$$

The first order term in (J.5) vanishes due to norm conservation, Eq. (I.2). The second order term can be rewritten by use of the compressibility sum rule (H.43),

$$\begin{aligned}
&T_{\rm s}^{\rm RLDA}[n_0+\delta j^0]+E_{\rm xc}^{\rm RLDA}[n_0+\delta j^0]\\
&=\int d^3r\,[t_{\rm s}(n_0)+e_{\rm xc}(n_0)]-\frac{1}{2}\int\frac{d^3q}{(2\pi)^3}\,\frac{\delta j^0(\boldsymbol{q})\;\delta j^0(-\boldsymbol{q})}{\Pi_{\rm L}^{(0)}(0,\boldsymbol{0})}.
\end{aligned} \tag{J.6}$$

The second order term in (J.6) has to be subtracted from the complete inhomogeneity correction (J.4) as it is already contained in the RLDA,

$$\begin{aligned}
\delta\tilde{T}_{\rm s}^{\rm LR}+\delta\tilde{E}_{\rm xc}^{\rm LR}=-\frac{1}{2}\int\frac{d^3q}{(2\pi)^3}\left\{\delta j^0(\boldsymbol{q})\left[\frac{1}{\Pi_{\rm L}(0,\boldsymbol{q})}-\frac{1}{\Pi_{\rm L}(0,\boldsymbol{0})}\right]\delta j^0(-\boldsymbol{q})\right.\\
\left.+\frac{\boldsymbol{j}(\boldsymbol{q})\cdot\boldsymbol{j}(-\boldsymbol{q})}{\Pi_{\rm T}(0,\boldsymbol{q})}\right\}.
\end{aligned} \tag{J.7}$$

Equation (J.7) explicitly demonstrates the current-dependence of relativistic density functionals. However, at this point $\delta\tilde{T}_{\rm s}^{\rm LR}$ and $\delta\tilde{E}_{\rm xc}^{\rm LR}$ are given as functionals of n_0 (inside $\Pi_{\rm L/T}$) and δj^0, but not yet as functionals of the complete density $j^0=n_0+\delta j^0$. Two paths can be followed towards the construction of actual density functionals: on the one hand, one can rewrite (J.7) as a fully nonlocal density functional utilizing either that $j^0(\boldsymbol{x})-j^0(\boldsymbol{y})=\delta j^0(\boldsymbol{x})-\delta j^0(\boldsymbol{y})$ [6, 85] or that $\boldsymbol{\nabla}j^0(\boldsymbol{x})=\boldsymbol{\nabla}\delta j^0(\boldsymbol{x})$ [158] (compare Sect. 4.4.2). On the other hand, one can restrict oneself to a long-wavelength expansion of the response kernels in (J.7), assuming $\delta j^\mu(\boldsymbol{q})$ to be strongly localized around $\boldsymbol{q}=\boldsymbol{0}$, i.e. $\delta j^\mu(\boldsymbol{x})$ to be rather delocalized. The latter approach leads to gradient corrections.

However, due to the limited information available for the relativistic polarization functions $\Pi_{\mathrm{L/T}}$ no applications of (J.7) to E_{xc} have been reported so far. In order to illustrate the basic scheme of the gradient expansion we therefore consider T_{s}. After insertion of (H.39) and (H.40) into (J.7) and subsequent Fourier transformation one finds

$$\delta T_{\mathrm{s}}^{[2]} = \frac{1}{72m}\int d^3x\,\frac{1}{n_0\eta}\left[1+2\frac{\beta}{\eta}\mathrm{arsinh}(\beta)\right]\left[\boldsymbol{\nabla}\delta j^0(\boldsymbol{x})\right]^2 + \frac{3\pi}{4}\int d^3x\int d^3y\,\frac{1}{\mathrm{arsinh}(\beta)}\,\frac{\boldsymbol{j}(\boldsymbol{x})\cdot\boldsymbol{j}(\boldsymbol{y})}{|\boldsymbol{x}-\boldsymbol{y}|}\,, \tag{J.8}$$

where the long-wavelength expansion has been taken into account to order $\boldsymbol{q}^2$ (denoted by the superscript [2]—β,η are given by Eq. (H.42)) and current conservation has been used in the second term. In the first term on the right-hand side of (J.8) one can now utilize $\boldsymbol{\nabla}\delta j^0(\boldsymbol{x}) = \boldsymbol{\nabla} j^0(\boldsymbol{x})$ and, correct to second order, $k_{\mathrm{F}} = [3\pi^2 j^0(\boldsymbol{x})]^{1/3}$. However, the density-dependent prefactor $1/\mathrm{arsinh}(\beta)$ of the current component cannot be expressed unambiguously in terms of $j^0(\boldsymbol{x})$ as now two spatial variables are available. As in the case of the complete linear response corrections (J.7) one is left with a choice for this substitution.[1] If one abbreviates this (symmetric) function of $\boldsymbol{x}$ and $\boldsymbol{y}$ by $\bar{\beta}(\boldsymbol{x},\boldsymbol{y})$, one obtains

$$\delta T_{\mathrm{s}}^{[2]}[j] = \frac{1}{72m}\int d^3x\,\frac{[\boldsymbol{\nabla} j^0(\boldsymbol{x})]^2}{j^0(\boldsymbol{x})}\,\frac{1}{\eta}\left[1+2\frac{\beta}{\eta}\mathrm{arsinh}(\beta)\right] + \frac{3\pi}{4}\int d^3x\int d^3y\,\frac{1}{\mathrm{arsinh}(\bar{\beta}(\boldsymbol{x},\boldsymbol{y}))}\,\frac{\boldsymbol{j}(\boldsymbol{x})\cdot\boldsymbol{j}(\boldsymbol{y})}{|\boldsymbol{x}-\boldsymbol{y}|}\,, \tag{J.9}$$

where β is now understood as $\beta = [3\pi^2 j^0(\boldsymbol{x})]^{1/3}/m$ ($\eta = \sqrt{1+\beta^2}$). Equation (J.9) demonstrates that current density functionals are inherently nonlocal, even in the long-wavelength limit.

One should note that the vacuum parts of $\Pi^{(0)}_{\mathrm{L/T}}$ do not contribute to $\delta T_{\mathrm{s}}^{[2]}$ as the normalization condition (G.48) together with (H.32) suppresses any vacuum contribution of the order $\boldsymbol{q}^2$. On the other hand, $\Pi^{(0)}_{\mathrm{v,R}}$ does contribute to higher order inhomogeneity corrections (for details and a comparison with the real space gradient expansion of T_{s} see [532]).

In principle, this formalism can be extended to quadratic and cubic response, which allows the derivation of higher order gradient terms. In practice, however, the limited knowledge of the corresponding response functions restricts the usefulness of a first-principles determination of relativistic gradient corrections.

As a final point one should mention that gradient corrections to the relativistic $T_{\mathrm{s}}[n]$ have also been derived by real-space methods [764–766, 763, 767]. These gradient terms serve as an extension of the relativistic Thomas-Fermi model [761, 768], in which the many-body problem is approached by direct solution of the basic vari-

[1] In contrast to the linear response approach the real space gradient expansion of $T_{\mathrm{s}}[j]$ determines the current contribution to the second order gradient correction completely [763].

ational equation (8.72). A summary of results and details, as e.g. use of the renormalization procedure, can be found in [72, 532, 769, 770]. Expressing the noninteracting relativistic kinetic energy in terms of the density $n = j^0$,

$$T_{\rm s} = \int d^3x \left\{ t_{\rm s}^{[0]}[n] + t_{\rm s}^{[2]}[n] + t_{\rm s}^{[4]}[n] + \ldots \right\} , \tag{J.10}$$

one finds for the case of a purely electrostatic external potential (in contrast to the case of a full four potential) the expressions

$$t_{\rm s}^{[0]}[n] = \frac{(3\pi^2 n)^{5/3}}{\pi^2 m} \frac{1}{\beta} \left[\frac{1}{8} \left(\beta\eta^3 + \beta^3\eta - {\rm arsinh}\beta \right) - \frac{\beta^3}{3} \right] \tag{J.11}$$

$$t_{\rm s}^{[2]}[n] = \frac{1}{72m} \frac{(\nabla n)^2}{n\eta} \left[1 + 2\frac{\beta}{\eta} {\rm arsinh}\beta \right] . \tag{J.12}$$

The more complicated expression for $t_{\rm s}^{[4]}[n]$ will not be given here. The agreement of (J.11) with (H.45) and of (J.12) with the density-dependent contribution to (J.9) is obvious.

Results for atoms and molecules obtained by direct application of the variational principle (without the intermediary of orbitals) are not of chemical accuracy. The functionals can, however, be useful for obtaining reasonable estimates of properties of systems that can not be investigated in such detail, for instance systems in the astrophysical field. For this purpose, it is of interest to note, that a temperature-dependent version of the relevant functionals has been derived as well [771].

Appendix K
Gordon Decomposition

The starting point for the derivation of the Gordon decomposition of the spatial components of the relativistic four current operator,

$$\hat{j}^{\mu} = \hat{\psi}^{\dagger}\alpha^{\mu}\hat{\psi} \qquad (\alpha^{\mu} = \gamma^{0}\gamma^{\mu}) \,, \tag{K.1}$$

is the field equation satisfied by the field operators $\hat{\psi}$, i.e. the Dirac equation,

$$\left(i\hbar c\gamma^{\mu}\partial_{\mu} - mc^{2} - e\gamma^{\mu}A_{\mu}\right)\hat{\psi} = 0 \,, \tag{K.2}$$

in which the potential A^{μ} may be operator-valued (∂_{μ} is defined in Eq. (8.4)). Note, however, that all subsequent steps can equally well be gone through for a current expressed in terms of single-particle orbitals,

$$j^{\mu} = \sum_{k} \Theta_{k}\phi_{k}^{\dagger}\alpha^{\mu}\phi_{k} \,,$$

as long as the orbitals satisfy a differential equation of the type (K.2) (as, for instance, the KS spinors).

The hermitian conjugate of (K.2) is given by

$$\hat{\psi}^{\dagger}\gamma^{0}\left(-i\hbar c\gamma^{\mu}\overleftarrow{\partial_{\mu}} - mc^{2} - e\gamma^{\mu}A_{\mu}\right)\gamma^{0} = 0 \,, \tag{K.3}$$

as $(\gamma^{\mu})^{\dagger} = \gamma^{0}\gamma^{\mu}\gamma^{0}$. The vector bar over $\overleftarrow{\partial_{\mu}}$ indicates that the derivative acts on the field operator to its left. Contraction of the field equation (K.2) with $\hat{\psi}^{\dagger}\alpha^{k}$ and of its hermitian conjugate (K.3) with $\alpha^{k}\hat{\psi}$ gives

$$\begin{aligned}
\hat{\psi}^{\dagger}\alpha^{k}\left(i\hbar c\gamma^{\mu}\partial_{\mu} - mc^{2} - e\gamma^{\mu}A_{\mu}\right)\hat{\psi} &= 0 \\
\hat{\psi}^{\dagger}\gamma^{0}\left(-i\hbar c\gamma^{\mu}\overleftarrow{\partial_{\mu}} - mc^{2} - e\gamma^{\mu}A_{\mu}\right)\gamma^{0}\alpha^{k}\hat{\psi} &= 0 \,.
\end{aligned}$$

If one adds up both equations, one obtains

$$\hat{\psi}^\dagger \left[i\hbar c\gamma^0 \left(\gamma^k \gamma^\mu \partial_\mu - \gamma^\mu \gamma^k \overleftarrow{\partial_\mu} \right) - 2mc^2 \alpha^k - e\gamma^0 \left(\gamma^k \gamma^\mu + \gamma^\mu \gamma^k \right) A_\mu \right] \hat{\psi} = 0 \,.$$

In the next step the scalar products in Minkowski space are split into their space-time components, utilizing the commutation relations (8.7)–(8.9),

$$\begin{aligned} \hat{\psi}^\dagger \Big[& - i\hbar c \left(\gamma^k \partial_0 + \gamma^k \overleftarrow{\partial_0} \right) + i\hbar c\gamma^0 \left(\gamma^k \gamma^l \partial_l - \gamma^l \gamma^k \overleftarrow{\partial_l} \right) \\ & - 2mc^2 \alpha^k - 2e\gamma^0 A^k \Big] \hat{\psi} \;=\; 0 \,. \end{aligned}$$

At this point one can use

$$\begin{aligned} \gamma^k \gamma^l &= \frac{1}{2} \left(\left\{ \gamma^k, \gamma^l \right\} + \left[\gamma^k, \gamma^l \right] \right) \\ &= g^{kl} - i\varepsilon_{klj} \Sigma^j \qquad\qquad \text{with} \quad \Sigma^j \;=\; \begin{pmatrix} \sigma^j & 0 \\ 0 & \sigma^j \end{pmatrix} \end{aligned} \tag{K.4}$$

to obtain

$$\begin{aligned} - i\hbar c \partial_0 \left(\hat{\psi}^\dagger \gamma^k \hat{\psi} \right) + i\hbar c \hat{\psi}^\dagger \gamma^0 \left(\partial^k - \overleftarrow{\partial^k} \right) \hat{\psi} + \hbar c\, \varepsilon_{klj} \partial_l \left(\hat{\psi}^\dagger \gamma^0 \Sigma^j \hat{\psi} \right) \\ - 2mc^2 \hat{\psi}^\dagger \alpha^k \hat{\psi} - 2eA^k \hat{\psi}^\dagger \gamma^0 \hat{\psi} = 0 \,. \end{aligned}$$

Most of the individual terms in this equation are easily identified with established quantities. With the definitions[1]

$$\hat{j}^\mu \;=\; \left(\hat{n}, \frac{\hat{\boldsymbol{j}}}{c} \right) \tag{K.5}$$

$$\hat{\boldsymbol{j}}_\mathrm{p} = -\frac{i\hbar}{2m} \hat{\psi}^\dagger \gamma^0 \left(\overrightarrow{\boldsymbol{\nabla}} - \overleftarrow{\boldsymbol{\nabla}} \right) \hat{\psi} \tag{K.6}$$

$$\hat{\boldsymbol{m}} = \frac{e\hbar}{2mc} \hat{\psi}^\dagger \gamma^0 \boldsymbol{\Sigma} \hat{\psi} \tag{K.7}$$

$$\hat{\rho}_\mathrm{s} = \hat{\psi}^\dagger \gamma^0 \hat{\psi} \tag{K.8}$$

(note the additional factor of c which is included in the three-vector $\boldsymbol{j}$ as compared to the spatial components of j^μ!) for the paramagnetic current $\hat{\boldsymbol{j}}_\mathrm{p}$, the magnetization density $\hat{\boldsymbol{m}}$ and the scalar density $\hat{\rho}_\mathrm{s}$ one finds

$$- i\hbar c \partial_0 \left(\hat{\psi}^\dagger \boldsymbol{\gamma} \hat{\psi} \right) + 2mc \hat{\boldsymbol{j}}_\mathrm{p} + \frac{2mc^2}{e} \boldsymbol{\nabla} \times \hat{\boldsymbol{m}} - 2mc \hat{\boldsymbol{j}} - 2e\boldsymbol{A} \hat{\rho}_\mathrm{s} = 0 \,.$$

Extracting the spatial components of the current, one finally ends up with

[1] Note the relation between the gradient vector and the covariant components ∂_k,

$$\boldsymbol{\nabla} = \left(\frac{\partial}{\partial r^1}, \frac{\partial}{\partial r^2}, \frac{\partial}{\partial r^3} \right) = (\partial_1, \partial_2, \partial_3) \,.$$

$$\hat{\boldsymbol{j}} \;=\; -\frac{i\hbar}{2m}\partial_0\left(\hat{\psi}^\dagger\boldsymbol{\gamma}\hat{\psi}\right) + \hat{\boldsymbol{j}}_{\mathrm{p}} + \frac{c}{e}\boldsymbol{\nabla}\times\hat{\boldsymbol{m}} - \frac{e}{mc}\boldsymbol{A}\hat{\rho}_{\mathrm{s}}\,. \tag{K.9}$$

In the case of stationary systems the first operator on the right-hand side does not contribute to any expectation value of $\hat{\boldsymbol{j}}$,

$$\langle\Psi_0|\hat{\boldsymbol{j}}|\Psi_0\rangle \;=\; \langle\Psi_0|\hat{\boldsymbol{j}}_{\mathrm{p}}|\Psi_0\rangle + \frac{c}{e}\boldsymbol{\nabla}\times\langle\Psi_0|\hat{\boldsymbol{m}}|\Psi_0\rangle - \frac{e}{mc}\boldsymbol{A}\,\langle\Psi_0|\hat{\rho}_{\mathrm{s}}|\Psi_0\rangle\,. \tag{K.10}$$

Note that the precise definition of $\boldsymbol{A}$ (in particular, its sign) is determined by the differential equation (K.2).

Appendix L
Some Useful Formulae

The body of this text relies on the knowledge of a largish number of mathematical relations. A much abbreviated list is offered here.

- Laurent expansion, theorem of residues:
  A complex-valued function $f(z)$, which is analytic in the domain $\mathscr{D} \subset \mathbb{C}$ and has an isolated pole of k-th order at a point z_0 enclosed by $\mathscr{D}$, can be expanded for all $z \in \mathscr{D}$ as (Laurent expansion)

$$f(z) = \sum_{n=-\infty}^{\infty} a_n (z - z_0)^n \,, \tag{L.1}$$

  with the coefficients a_n given by

$$a_n = \oint_{\mathscr{C}} \frac{dz'}{2\pi i} \frac{f(z')}{(z' - z_0)^{n+1}} \,. \tag{L.2}$$

  Here the closed path $\mathscr{C}$ is contained fully in the domain, has a counterclockwise orientation, and encloses z_0, but no other singular point. The coefficient a_{-1}, the residue, is given by

$$a_{-1} = \oint_{\mathscr{C}} \frac{dz}{2\pi i} f(z) \,. \tag{L.3}$$

  A generalization to the case that the path encloses a set of isolated poles is the theorem of residues,

$$\oint_{\mathscr{C}} \frac{dz}{2\pi i} f(z) = \text{sum of the residues of all poles enclosed by } \mathscr{C} \,. \tag{L.4}$$

  A prominent example for the application of (L.4) is the contour integral representation of the step function,

$$\Theta(x) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} \frac{e^{i\omega x}}{\omega - i\eta} \,, \tag{L.5}$$

which is used to implement the time-ordering required for many response and Green's functions in frequency space.

- Dirac identity:
  For integrations over frequency often the integral representation of the δ-function,

$$\delta(x) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{i\omega x}, \tag{L.6}$$

  or the Dirac identity,

$$2\pi i\,\delta(x) = \frac{1}{x-i\eta} - \frac{1}{x+i\eta} \tag{L.7}$$

$$\frac{1}{x-i\eta} = \mathscr{P}\frac{1}{x} + \pi i\,\delta(x) \tag{L.8}$$

$$\frac{1}{x+i\eta} = \mathscr{P}\frac{1}{x} - \pi i\,\delta(x) \tag{L.9}$$

  is used ($\mathscr{P}$ denotes the Cauchy principal value integral).
- Fourier representation of Coulomb interaction:
  Whenever the Coulomb interaction has to be integrated over the complete space, use of the following regularized form is necessary

$$\int \frac{d^3q}{(2\pi)^3} \frac{e^{i\boldsymbol{q}\cdot\boldsymbol{r}}}{\boldsymbol{q}^2+\mu^2} = \frac{e^{-\mu|\boldsymbol{r}|}}{4\pi|\boldsymbol{r}|}. \tag{L.10}$$

- General identities for commutators:

$$[\hat{A}\hat{B},\hat{C}] = \hat{A}[\hat{B},\hat{C}] + [\hat{A},\hat{C}]\hat{B} \tag{L.11}$$

$$e^{\hat{A}}\,\hat{B}\,e^{-\hat{A}} = \sum_{n=0}^{\infty} \frac{1}{n!} \underbrace{\left[\hat{A},\left[\hat{A},\left[\ldots\left[\hat{A},\hat{B}\right]\right]\ldots\right]\right]}_{n \text{ times}}. \tag{L.12}$$

- Commutators involving field operators:
  The following basic commutator of four field operators can be derived directly from the anticommutation rules (2.6) and (2.7),

$$\begin{aligned}&\left[\hat{\psi}^\dagger(\boldsymbol{r}_1\sigma_1)\hat{\psi}(\boldsymbol{r}_2\sigma_2), \hat{\psi}^\dagger(\boldsymbol{r}_3\sigma_3)\hat{\psi}(\boldsymbol{r}_4\sigma_4)\right]\\ &= -\delta^{(3)}(\boldsymbol{r}_1-\boldsymbol{r}_4)\,\delta_{\sigma_1\sigma_4}\hat{\psi}^\dagger(\boldsymbol{r}_3\sigma_3)\hat{\psi}(\boldsymbol{r}_2\sigma_2)\\ &\quad +\delta^{(3)}(\boldsymbol{r}_2-\boldsymbol{r}_3)\,\delta_{\sigma_2\sigma_3}\hat{\psi}^\dagger(\boldsymbol{r}_1\sigma_1)\hat{\psi}(\boldsymbol{r}_4\sigma_4).\end{aligned} \tag{L.13}$$

  Use of this result leads to

$$0 = \left[\hat{\psi}^\dagger(\boldsymbol{r}\sigma)\hat{\psi}(\boldsymbol{r}\sigma), \hat{\psi}^\dagger(\boldsymbol{r}'\sigma')\hat{\psi}(\boldsymbol{r}'\sigma')\right] \tag{L.14}$$

$$0 = \left[\int d^3r\,\hat{\psi}^\dagger(\boldsymbol{r}\sigma)\nabla^2\hat{\psi}(\boldsymbol{r}\sigma), \int d^3r'\,\hat{\psi}^\dagger(\boldsymbol{r}'\sigma')\hat{\psi}(\boldsymbol{r}'\sigma')\right] \tag{L.15}$$

$$0 = \left[\hat{\psi}^\dagger(\boldsymbol{r}\sigma)\hat{\psi}(\boldsymbol{r}\sigma)\hat{\psi}^\dagger(\boldsymbol{r}'\sigma')\hat{\psi}(\boldsymbol{r}'\sigma'), \hat{\psi}^\dagger(\boldsymbol{r}''\sigma'')\hat{\psi}(\boldsymbol{r}''\sigma'')\right]$$
$$= \left[\hat{\psi}^\dagger(\boldsymbol{r}\sigma)\hat{\psi}^\dagger(\boldsymbol{r}'\sigma')\hat{\psi}(\boldsymbol{r}'\sigma')\hat{\psi}(\boldsymbol{r}\sigma), \hat{\psi}^\dagger(\boldsymbol{r}''\sigma'')\hat{\psi}(\boldsymbol{r}''\sigma'')\right]. \quad \text{(L.16)}$$

With the relation (L.13) one can also evaluate the commutator of the density (2.4) and the paramagnetic current (2.158)

$$\left[\hat{\boldsymbol{j}}_\mathrm{p}(\boldsymbol{r}), \hat{n}(\boldsymbol{r}')\right] = \frac{-i\hbar}{2m}\left[\boldsymbol{\nabla}\delta^{(3)}(\boldsymbol{r}-\boldsymbol{r}')\right]\sum_\sigma\left[\hat{\psi}^\dagger(\boldsymbol{r}\sigma)\hat{\psi}(\boldsymbol{r}'\sigma) + \hat{\psi}^\dagger(\boldsymbol{r}'\sigma)\hat{\psi}(\boldsymbol{r}\sigma)\right]$$
$$+\frac{i\hbar}{2m}\,\delta^{(3)}(\boldsymbol{r}-\boldsymbol{r}')\,\boldsymbol{\nabla}\hat{n}(\boldsymbol{r}). \quad \text{(L.17)}$$

Similarly, one obtains for the commutator of the kinetic energy and density operators

$$\left[\hat{T}, \hat{n}(\boldsymbol{r})\right] = i\hbar\,\boldsymbol{\nabla}\cdot\hat{\boldsymbol{j}}_\mathrm{p}(\boldsymbol{r}). \quad \text{(L.18)}$$

- Pauli matrices:
  The basic commutators (anticommutators) of the Pauli matrices,

$$[\sigma_i, \sigma_j] = 2i\sum_k \varepsilon_{ijk}\,\sigma_k \quad \text{(L.19)}$$
$$\left\{\sigma_i, \sigma_j\right\} = 2\delta_{ij}, \quad \text{(L.20)}$$

  indicate that these operators are generators of the group $SU(2)$. The matrices are hermitian $\sigma_i^\dagger = \sigma_i$. These properties, together with a statement on the two eigenvalues of σ_z, allows the determination of an explicit representation

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad \text{(L.21)}$$

  For handling Pauli matrices the following identity is often helpful,

$$(\boldsymbol{\sigma}\cdot\boldsymbol{a})\,(\boldsymbol{\sigma}\cdot\boldsymbol{b}) = \boldsymbol{a}\cdot\boldsymbol{b} + i\,\boldsymbol{\sigma}\cdot(\boldsymbol{a}\times\boldsymbol{b}), \quad \text{(L.22)}$$

  which can be derived from the basic commutators.
  The corresponding commutation relations of the relativistic (4×4) Pauli matrices (8.138) are

$$\left[\Sigma^i, \Sigma^j\right] = 2i\sum_k \varepsilon_{ijk}\,\Sigma^k \quad \text{(L.23)}$$
$$\left\{\Sigma^i, \Sigma^j\right\} = -2g^{ij}. \quad \text{(L.24)}$$

  A standard representation is

$$\boldsymbol{\Sigma} = \begin{pmatrix} \boldsymbol{\sigma} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\sigma} \end{pmatrix}. \quad \text{(L.25)}$$

- Feynman rules:
  These rules define the transition between the Feynman diagrams representing the individual contributions to the perturbation expansion of Green's functions (and all quantities related to them) and the corresponding analytical expressions. They are set up here in a rather general form which allows a coherent treatment of all kinds of (sub)diagrams in real space, including diagrams contributing to n-point functions such as the self-energy and the response function. The critical diagrams which require this extended form are those for which there are vertices to which only a single line (electron or interaction) is attached, as for instance the first order self-energy (3.125).
  The four basic elements of Feynman diagrams representing the perturbation expansion for inhomogeneous systems are:

  – The noninteracting (as for instance the KS) Green's function (3.124),

$$G_0(\boldsymbol{r}\sigma t,\boldsymbol{r}'\sigma' t') = \int \frac{d\omega}{2\pi}\, e^{-i\omega(t-t')}\, G_0(\boldsymbol{r}\sigma,\boldsymbol{r}'\sigma',\omega) \tag{L.26}$$

$$= \boldsymbol{r}'\sigma' t' \longrightarrow \boldsymbol{r}\sigma t$$

$$G_0(\boldsymbol{r}\sigma,\boldsymbol{r}'\sigma',\omega) = \sum_l \left\{ (1-\Theta_l)\frac{\phi_l(\boldsymbol{r}\sigma)\phi_l^*(\boldsymbol{r}'\sigma')}{\omega-\varepsilon_l/\hbar+i\eta} + \Theta_l \frac{\phi_l(\boldsymbol{r}\sigma)\phi_l^*(\boldsymbol{r}'\sigma')}{\omega-\varepsilon_l/\hbar-i\eta} \right\}.$$

  – The Coulomb interaction, suitably extended to the time domain, in order to simplify the rules,

$$w(\boldsymbol{r}-\boldsymbol{r}',t-t') \;=\; \delta(t-t')\,\frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|} \;=\; \boldsymbol{r}'t' \sim\sim \boldsymbol{r}t \quad . \tag{L.27}$$

  – The simple vertex, drawn as a bold dot,

    The lines attached to the dot only serve as an indication that there are (at most) two solid and one wiggly line connected to a single vertex.
  – If present, an additional perturbing external potential,

$$v_{\mathrm{ext}}(\boldsymbol{r}) = \; \boldsymbol{r}t \sim\sim\times \tag{L.28}$$

  Any given Feynman diagram is translated into an algebraic expression according to the following rules:

  1. Distinguish between simple endpoints of lines (be it solid or wiggly), i.e. endpoints not attached to a bold dot, and endpoints at vertices, characterized by the bold dot. The former endpoints will be called external points in the following, the latter internal endpoints.

2. Distinguish between internal vertices, at which one incoming and one outgoing solid (electron) line and one wiggly (interaction) line meet, and external vertices, at which one or two of these attached lines are missing.
3. Label all vertices and external points by some number i.
4. Replace each directed solid line for which the arrow points from a vertex or an external point j to a vertex or an external point i by $G_0(\boldsymbol{r}_i\sigma_i t_i, \boldsymbol{r}_j\sigma_j t_j)$.
5. Replace each wiggly line connecting the vertices or external points i and j by $w(\boldsymbol{r}_i - \boldsymbol{r}_j, t_i - t_j)$ (the direction plays no role, as the interaction is symmetric under exchange of its arguments).
6. Replace each wiggly line with a cross at its end attached to vertex i by $v_{\mathrm{ext}}(\boldsymbol{r}_i)$.
7. Replace each external vertex i with only one line attached by

$$\delta^{(3)}(\boldsymbol{r}_i - \boldsymbol{r}_{i'})\,\delta(t_i - t_{i'})\,\delta_{\sigma_i,\sigma_{i'}}\ .$$

   The space-time labels $\boldsymbol{r}_i t_i$ and $\boldsymbol{r}_{i'} t_{i'}$ are two of the arguments of the n-point function to which the diagram contributes. The same applies to both spin labels, if a wiggly line is attached to the vertex. On the other hand, if a solid line is attached to the vertex, the spin label σ_i is the spin index of this internal solid line attached, while $\sigma_{i'}$ denotes a spin argument of the n-point function.
8. Integrate over all coordinates and times associated with internal vertices,

$$\int d^3 r_i\, dt_i\ ,$$

   and sum over all spins associated with internal endpoints of solid lines.
9. If the rules lead to Green's functions G_0 for which both time arguments coincide, $t_i = t_j = t$, interpret these functions as $G_0(\boldsymbol{r}_i\sigma_i t, \boldsymbol{r}_j\sigma_j t + \eta)$ and take the limit $\eta \to 0^+$ at the end of the calculation. This can only happen if the solid line ends at the same point as it starts, or if the start and end point of G_0 are connected by a single interaction line. This procedure ensures the proper operator ordering of $\hat{\psi}_0$ and $\hat{\psi}_0^\dagger$ at equal times.
10. Multiply the resulting expression by a factor of

$$(-i/\hbar)^{n+m}\, i^l\, (-1)^F$$

    for a diagram which contains n interaction, m external potential and l electron lines as well as F closed loops of solid lines.
11. Adjust the overall prefactor to the quantity (Green's or response function, density, energy, ...) which is evaluated, in accordance with the definition of this quantity. In the case of an energy (or vacuum amplitude) diagram take care of the multiplicities involved (see e.g. [95]).

For a homogeneous system, for which no external potential is present, a representation in momentum space is the appropriate choice. The three remaining basic elements after Fourier transformation are:

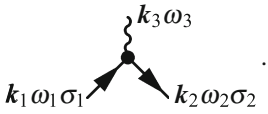
– The noninteracting Green's function:

$$G_0(\boldsymbol{k},\omega,\sigma\sigma') = \delta_{\sigma\sigma'}\left[\frac{\Theta(|\boldsymbol{k}|-k_\mathrm{F})}{\omega-\varepsilon_k/\hbar+i\eta}+\frac{\Theta(k_\mathrm{F}-|\boldsymbol{k}|)}{\omega-\varepsilon_k/\hbar-i\eta}\right] = \quad \boldsymbol{k}\omega\sigma \quad . \tag{L.29}$$

– The Coulomb interaction (in the screened form given above):

$$w(\boldsymbol{q}) = \frac{4\pi e^2}{\boldsymbol{q}^2+\mu^2} \quad = \quad \boldsymbol{q} \quad . \tag{L.30}$$

– The simple vertex:



. (L.31)

The Feynman rules for a distinct diagram are in this case:

1. Assign a direction to each interaction (wiggly) line; associate energy (ω) and momentum to each line (be it solid or wiggly) and conserve energy and momentum at each vertex.
2. Replace each directed solid line for which the arrow points from vertex or external point j to vertex or external point i by $G_0(\boldsymbol{k},\omega,\sigma_i\sigma_j)$.
3. If a solid line ends at the same point as it starts, or if the start and end point of a solid line are connected by a single interaction line, interpret the associated G_0 as $e^{i\omega\eta}G_0(\boldsymbol{k},\omega,\sigma_i\sigma_j)$ and take the limit $\eta\to 0^+$ at the end of the calculation.
4. Replace each wiggly line by $w(\boldsymbol{q})$.
5. Wherever two solid lines meet at some vertex conserve the spin σ at the vertex and sum over σ.
6. Integrate over all energies and momenta which do not correspond to arguments of the Green's or n-point function.
7. Multiply the resulting expression by a factor of

$$(-i/\hbar)^{n+m}\,i^l\,(-1)^F$$

   for a diagram which contains n interaction, m external potential and l electron lines as well as F closed loops of solid lines.
8. Adjust the overall prefactor to the quantity (Green's or response function, density, energy, ...) which is evaluated, in accordance with the definition of this quantity. In the case of an energy (or vacuum amplitude) diagram take care of the multiplicities involved.

These rules are identical with those given in [94], Chaps. 9–12.

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