

Functional representation of correlations in inhomogeneous many-electron systems

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We discuss the Legendre conjugate of the Hohenberg-Kohn energy-density functional, i.e., the total energy of an inhomogeneous many-electron system, considered as a functional of the external Coulomb potential (the nuclear Coulomb skeleton of a molecule, for instance) as the starting point of an alternative formulation of a theory of electronic correlations. We then relate this functional to the nonrelativistic or relativistic microscopic many-body theory. The essential bridge between the two theories is many-body perturbation theory perturbing around a mean field. We then point out that a particular choice for the latter, the g -Hartree mean field, leads to a transparent physical picture: The relevant functional of the external field, $g_0 - 1$, representing electronic correlations, is interpreted as a polarization charge density induced by the latter. This picture, in turn, leads to a Clausius-Mosotti type of equation for this correlation functional. Applications to atomic- and molecular-structure calculations are discussed.

I. INTRODUCTION

Coulomb correlations in inhomogeneous many-electron systems, atoms, and molecules, for instance, are usually accounted for theoretically by one of the following approaches. The first alternative is based on a microscopic theory starting from the quantum-mechanical equation of motion, e.g., the Schrödinger equation for nonrelativistic systems. After invoking the Born-Oppenheimer approximation for molecules, which effectively decouples electronic degrees of freedom and those of the nuclear skeleton, the first level of theory is conveniently chosen to provide an effective single-particle description of the electronic structure, and usually the Hartree-Fock approximation is chosen for this purpose. The underlying physical picture is an assembly of quasi-particles moving independently in the mean field furnished by the electrons and the external field caused by the nuclei. Deviations of the values of observables in the Hartree-Fock mean-field theory from those of the exact theory are termed correlations in a more restricted sense. They are in turn calculable by various methods developed in the past few decades,¹ which may be classified as either perturbative or variational, the latter often in the form of configuration-interaction (CI) treatments, which in the case of a "full CI" yields an exact solution of the many-particle problem in a model space defined by a suitable tensor product of one-particle spaces of finite dimensions.

Common to both methods is the problem of convergence of the corresponding expansions of which only the first few terms can be calculated, practically speaking. Parallel to the question of practicality another problem also common to both methods emerges: A physical interpretation of correlations is counterintuitive and cumbersome, since the latter are parametrized by millions of CI

expansion coefficients or individual diagrams in the perturbation series.

The second alternative for an attempt to solve the problem of correlations is based on the Hohenberg-Kohn theorem, which tells us that the exact electron density $n(\mathbf{x})$ determines the total energy by means of a universal, albeit unknown, functional of $n(\mathbf{x})$. In the framework of density-functional theory² practical applications are commonly carried out in form of a local-density approximation. A Kohn-Sham-type equation² defines an effective single-particle picture that includes the correlations from the beginning; the unknown density functional is approximated by an educated guess based on results known from the homogeneous electron gas.

One of the goals of the present paper is to provide a link between density-functional theory and the quantum theories of the first type sketched above, i.e., to develop a method to parametrize Coulomb correlations by means of a function of spatial coordinates which is, of course, functionally dependent on the external nuclear Coulomb potential $\mu(\mathbf{x})$ since changing the latter implies altering correlations. The ensuing functional $g_0[\mu(\mathbf{x})](\mathbf{x})$ is linked to the microscopic theory by virtue of its occurrence as an effective coupling constant in a mean-field equation (namely the g -Hartree equation) for the quantum system under investigation.

It turns out that for a given configuration the functional derivative of $g_0[\mu(\mathbf{x})]$ with respect to $\mu(\mathbf{x})$ can be interpreted as a polarization charge density, whereas suitable integrals over higher functional derivatives describe a correlation charge density. The sum of the quasiparticle charge density $\sum_{\alpha} n_{\alpha} |\psi_{\alpha}(\mathbf{x})|^2$ and the polarization density equals the static charge density $n(\mathbf{x})$, which is the source of the static electric field [the $\psi_{\alpha}(\mathbf{x})$ denote g -Hartree single-particle orbitals]; the electric field seen by an elec-

tron bound in the many-electron system under consideration (and, hence, the force acting on it), on the other hand, results from the charge distribution which is composed of $n(\mathbf{x})$ and, in addition, of the correlation charge density. The construction of the latter remotely follows in spirit the derivation of the Clausius-Mosotti² and Lorenz-Lorentz³ formulas. These notions together with the above-mentioned interpretation of $g_0[\mu](\mathbf{x})$ as an effective coupling constant lead to a functional differential equation for $g_0[\mu](\mathbf{x})$.

We then develop a formalism for the calculation of the response of a correlated charge density to external perturbations. In quantum chemistry, the same goal is accomplished by considering the derivatives of the parameters of the correlations treatment (e.g., the CI coefficients and the single-particle orbitals used for the CI expansion) with respect to an external perturbation.⁴

The equations for derivatives of, e.g., g -Hartree orbitals with respect to the external field, are comparable to the coupled perturbed Hartree-Fock equations.⁵ Our approach is, however, more general in that (i) we consider arbitrary variations of the external field by means of the technique of functional derivation, and (ii) we calculate the response of a *correlated* charge density. We thus have additional terms in the coupled perturbed equations, referring to (functional) derivatives of the aforementioned functional $g_0[\mu(\mathbf{x})]$ which is to be determined from its functional differential equation.

We do not touch questions like the precise specifications of the domain on which $g_0[\mu]$ is defined nor do we try to set up an algorithm for an explicit construction of the Legendre transform of the Hohenberg-Kohn functional to a functional of the external potential $\mu(\mathbf{x})$.⁶ The scenario we have in mind is a different one: an ansatz for the functional $g_0[\mu]$ which is stringently constrained by our Clausius-Mosotti type of equation is tested by many-body perturbation theory—in the ideal case it should sum up to zero by the very definition of $g_0[\mu]$. Having thus found a reliable parametrization for correlations in terms of g_0 we proceed to calculate further physical observables by computing higher-order response to variations of the external potential $\mu(\mathbf{x})$ and, if required, by many-body perturbation theory in the corresponding g -Hartree basis. Numerical studies of this scheme are deferred to a planned subsequent paper.

The paper is organized as follows. After an analysis of the energy functional for atoms and molecules, we present the mean-field construction of this energy functional using $g_0[\mu(\mathbf{x})]$ and the g -Hartree equation. A discussion also addressing lines of further development and generalizations concludes the paper. Technical details of the derivations in Secs. II and III are given in an Appendix.

II. THE ENERGY FUNCTIONAL FOR ATOMS AND MOLECULES

The total energy E_{tot} of an inhomogeneous many-electron system certainly depends on the external field producing the inhomogeneity. We express this dependence by writing E_{tot} as a functional of the external field

$\mu(\mathbf{x})$,

$$E_{\text{tot}} = E_{\text{tot}}[\mu(\mathbf{x})]. \quad (2.1)$$

For atoms and molecules the external field $\mu(\mathbf{x})$ is identified, of course, with the Coulomb potential of the nucleus and the nuclear skeleton, respectively. (We shall adopt in the following the Born-Oppenheimer approximation and consider the nuclear skeleton of molecules as adiabatically quasistatic.) Another important case which we simply point out for the sake of illustration without treating it any further is the interaction of strong maser or laser fields with atoms and molecules; in a radiation gauge $\mu(\mathbf{x})$ is identified with the vector potential corresponding to whatever maser or laser modes interact.

The total energy of an electronic configuration of an atom or a molecule depends, of course, also on other variables. Within the Born-Oppenheimer approximation the following procedure for labeling an interacting many-electron state, *all* correlations included, is assumed to be viable: we start from an (antisymmetric) product state Ψ_0 of single-particle orbitals $|\alpha\rangle$ labeled by quantum numbers α ,

$$\Psi_0 = \prod_{\alpha} \otimes (|\alpha\rangle)^{n_{\alpha}}, \quad (2.2)$$

where

$$n_{\alpha} = \begin{cases} 1, & \text{occupied} \\ 0, & \text{unoccupied} \end{cases}$$

indicates whether $|\alpha\rangle$ is occupied or unoccupied, and build up the interacting many-electron state by including correlations perturbatively

$$\Psi_0 \rightarrow \Psi[\{n_{\alpha}\}], \quad (2.3)$$

thus obtaining a labeling of a fully correlated state Ψ by a set of occupation numbers $\{n_{\alpha}\}$ of single-electron states. We confine our discussion to cases that admit a description by means of a single string of occupation numbers $\{n_{\alpha}\}$, although it can be extended to a multiconfiguration procedure parametrized by a set of occupation number strings together with their mixing coefficients. Needless to say, as in all Born-Oppenheimer-type structure calculations the question remains whether these parameters describing the quantum state in question change adiabatically when the external potential is varied. We assume this to be the case, although the existence and viability of such an adiabatic change is far from being proven in any rigorous sense.

It is with this understanding that we now label the total energy of an electronic configuration as

$$E_{\text{tot}} = E_{\text{tot}}[\mu(\mathbf{x}); \{n_{\alpha}\}]. \quad (2.4)$$

A transition characterized by states long before and after the interaction

$$\Psi[\{n_{\alpha}^{\text{initial}}\}] \rightarrow \Psi[\{n_{\alpha}^{\text{final}}\}]$$

then induces a change of energy in the electronic configuration

$$\Delta E = E_{\text{tot}}[\mu^{\text{final}}(\mathbf{x}); \{n_{\alpha}^{\text{final}}\}] - E_{\text{tot}}[\mu^{\text{initial}}(\mathbf{x}); \{n_{\alpha}^{\text{initial}}\}] . \quad (2.5)$$

It is important to observe that the functional (2.1) or, specified for atoms and molecules, (2.4) is nothing but a grand-canonical version of the energy-density functional originally introduced and elaborated by Hohenberg, Kohn, and Sham.² Indeed, since $\mu(\mathbf{x})$ as the fourth component of the gauge four-potential can be viewed as a space-dependent chemical potential, the space dependence reflecting the inhomogeneity of the many-electron system under consideration, we obtain via thermodynamical analogy the electronic charge density as

$$n(\mathbf{x}) = \frac{\delta E_{\text{tot}}}{\delta \mu(\mathbf{x})} . \quad (2.6)$$

The charge density $n(\mathbf{x})$ and the potential $\mu(\mathbf{x})$ appear as Legendre conjugates; inverting (2.6) in order to obtain the energy-density functional involves in practical cases the local-density approximation.⁷

Our point of view, which we shall expand in the following, is that the use of the nuclear Coulomb skeleton potential as an external variable $\mu(\mathbf{x})$ to express functional dependencies of the total energy has considerable practical advantages for the theoretical description of molecules. In particular, we shall describe a construction of the functional (2.4) in which *all* correlations due to the electron-electron interaction are parametrized by a functional

$$g_0 = g_0[\mu(\mathbf{x}); \{n_{\alpha}\}] . \quad (2.7)$$

Our construction is close in spirit to the one originally proposed by Kohn and Sham:⁸ as the underlying concept we also employ the notion of a mean field. However, in our case the mean field is constructed such that, the correlation functional (2.7) given, the total energy E_{tot} , the charge density (2.6), all higher charge-charge correlations [$\hat{n}(\mathbf{x})$ is the charge-density operator]

$$\langle \hat{n}(\mathbf{x}_1) \hat{n}(\mathbf{x}_2) \cdots \hat{n}(\mathbf{x}_n) \rangle = \frac{1}{n!} \frac{\delta^n E_{\text{tot}}}{\delta \mu(\mathbf{x}_1) \delta \mu(\mathbf{x}_2) \cdots \delta \mu(\mathbf{x}_n)} , \quad (2.8)$$

etc., are exactly the ones predicted by the theory of inhomogeneous many-electron systems (i.e., nonrelativistic or relativistic quantum electrodynamics). Of course, strictly speaking, this statement, taken literally as it stands is just a tautology; we simply shifted the problem of determining the functional E_{tot} to the determination of the functional g_0 . From the point of view of perturbation theory this is not quite as trivial as it sounds since $1 - g_0$ is of the order of the strength of the electron-electron interaction and all single-particle contributions to (2.4), (2.6), and (2.8) are taken into account (as in every Kohn-Sham-type construction).

Furthermore, as we shall see in the following our mean field incorporates indirect knowledge of correlations via the functional g_0 . Hence, even if we do not know the functional g_0 exactly we can nonetheless develop phenomenologically guided Ansätze for g_0 : the closer we get

to the exact form the more rapidly many-body perturbation theory⁹ (MBPT) will converge since, by construction, all perturbative contributions vanish for the exact g_0 .

In the following we shall develop this mean-field theory for E_{tot} , the charge density, and density-density correlations. We shall put particular emphasis on deriving general constraints on the functional g_0 which will prove useful in the search for efficient parametrizations.

III. MEAN-FIELD CONSTRUCTION OF THE ENERGY FUNCTIONAL

The g -Hartree mean-field theory provides an efficient scheme for the construction of the functional (2.4) which allows for a transparent physical interpretation and, thus, for a parametrization which follows simple physical guidelines directly interpretable in terms of observable physical parameters.

At the center is the g -Hartree mean-field potential

$$\mathcal{V}_g(\mathbf{x}) = \int d^3x' V(\mathbf{x}, \mathbf{x}') \sum_{\alpha} n_{\alpha} [g |\psi_{\alpha}(\mathbf{x}')|^2 - (1-g) \psi_{\alpha}^*(\mathbf{x}') \psi_{\alpha}(\mathbf{x})^*] , \quad (3.1)$$

where

$$V(\mathbf{x}, \mathbf{x}') = \frac{e^2}{4\pi |\mathbf{x} - \mathbf{x}'|} \quad (3.2)$$

is the electron-electron Coulomb interaction and $*$ denotes the usual exchange convolution operation; the sum involves occupied states. This potential was derived from a stationarity condition¹⁰ and a variational procedure,¹¹ the important point to note is that this potential is not unique but rather a one-parameter set parametrized by g which, for the sake of generality, we take as space dependent,

$$g = g(\mathbf{x}) , \quad (3.3)$$

in Eq. (3.1).

The single-particle orbitals are to be determined self-consistently from the g -Hartree equations

$$[D + \mathcal{V}_g(\mathbf{x})] \psi_{\alpha}(\mathbf{x}) = \varepsilon_{\alpha} \psi_{\alpha}(\mathbf{x}) , \quad (3.4)$$

the single-particle dispersion can be taken as

$$D = -\frac{1}{2m} \Delta + \mu(\mathbf{x}) \quad (3.5)$$

or

$$D = -i\alpha \cdot \partial + m\beta + \mu(\mathbf{x}) \quad (3.6)$$

for the nonrelativistic and the relativistic case, respectively, $\mu(\mathbf{x})$ is the external potential seen by the particle at \mathbf{x} and constitutes the functional variable described in Sec. II.

The parameter g will now be chosen¹² such that

$$E_{\text{tot}} = E_{g-H} |_{g=g_0} , \quad (3.7)$$

i.e., that the total energy (2.4) is exactly equal to the g -

Hartree single-particle energy E_{g-H}

$$E_{g-H} = \sum_{\alpha} n_{\alpha} \varepsilon_{\alpha} - \sum_{\beta} n_{\beta} \mathcal{V}_{g\beta}^{\beta} \quad (3.8)$$

where

$$\mathcal{V}_{g\beta}^{\alpha} = \frac{1}{2} \int d^3x' \psi_{\alpha}^{*}(\mathbf{x}') \mathcal{V}_g(\mathbf{x}') \psi_{\beta}(\mathbf{x}') . \quad (3.9)$$

Of course, Eq. (3.7) determines g_0 as a functional of $\mu(\mathbf{x})$ and the configuration $\{n_{\alpha}\}$ once the space dependence (3.3) is prescribed:

$$g_0 = g_0[\mu(\mathbf{x}); \{n_{\alpha}\}] , \quad (3.10)$$

or, denoting the \mathbf{x} dependence explicitly,

$$g_0(\mathbf{x}) = g_0[\mu; \{n_{\alpha}\}](\mathbf{x}) . \quad (3.11)$$

This construction might appear confusing; we shall try to be more precise by using mathematical icons. Let the map (3.3)

$$g: \mathbb{R}^3 \rightarrow \mathbb{R}$$

be parametrized by parameters $\gamma_0, \gamma_1, \dots, \gamma_k$. Equation (3.7) then fixes one parameter, γ_0 , say, as a functional of $\mu(\mathbf{x})$ and $\{n_{\alpha}\}$, i.e., as a map

$$\gamma_0: \{\mu(\mathbf{x})\} \times \{n_{\alpha}\} \rightarrow \mathbb{R} , \quad (3.12)$$

where $\{\mu(\mathbf{x})\}$ denotes the set of admissible potentials. Inserting this map into the chosen parametrization for g we obtain the functional (3.10) or (3.11). The remaining parameters $\gamma_1, \dots, \gamma_k$ are not fixed by (3.7) and play the role of dummy parameters: as long as they are chosen within physically reasonable boundaries the results presented below, in principle, do not depend on their choice. On the other hand, a physically viable ansatz for the function (3.3) will certainly increase the speed of convergence of MBPT which we shall use to compensate the practically unavoidable incompleteness of the construction of the functional (3.12) and (3.10) or (3.11). Anyway, we should remember that the choice (3.3) for $g(\mathbf{x})$ is essentially arbitrary and can be restricted by condition (3.7). In the following we shall show that this restriction leads to a physically intriguing picture of correlations in atoms and especially in molecules.

To this end we calculate the charge density $n(\mathbf{x})$ defined in (2.6) (for details we refer to the Appendix)

$$n(\mathbf{x}) = \frac{\delta E_{\text{tot}}}{\delta \mu(\mathbf{x})} = \sum_{\alpha} n_{\alpha} |\psi_{\alpha}(\mathbf{x})|^2 + \left\langle \frac{\delta g_0}{\delta \mu(\mathbf{x})} \right\rangle_{\text{pol}} , \quad (3.13)$$

where

$$\left\langle \frac{\delta g_0}{\delta \mu(\mathbf{x})} \right\rangle_{\text{pol}} = \frac{1}{2} \sum_{\alpha} n_{\alpha} \mathcal{W}_{\text{pol}\alpha}^{\alpha} \quad (3.14)$$

and

$$\mathcal{W}_{\text{pol}\beta}^{\alpha} = \int d^3x' \psi_{\alpha}^{*}(\mathbf{x}') \frac{\delta g_0}{\delta \mu(\mathbf{x})}[\mu; \{n_{\alpha}\}](\mathbf{x}') \mathcal{V}_{\text{pol}}(\mathbf{x}') \psi_{\beta}(\mathbf{x}') \quad (3.15)$$

with

$$\mathcal{V}_{\text{pol}}(\mathbf{x}) = \sum_{\alpha} n_{\alpha} \int d^3x' V(\mathbf{x}, \mathbf{x}') \times [|\psi_{\alpha}(\mathbf{x}')|^2 + \psi_{\alpha}^{*}(\mathbf{x}') \psi_{\alpha}(\mathbf{x})] . \quad (3.16)$$

This equation has a natural physical interpretation: $n(\mathbf{x})$, defined in (2.6) and, hence, originating from the equation of motion has to be considered as the source of the electric field exerting a mechanical force on the electrons building up the atom or molecule. Thus,

$$\nabla \cdot \mathbf{E} = 4\pi n(\mathbf{x}) ; \quad (3.17)$$

defining now

$$\nabla \cdot \mathbf{D} = 4\pi \rho(\mathbf{x}), \quad \nabla \cdot \mathbf{P} = \rho_{\text{pol}}(\mathbf{x}) , \quad (3.18)$$

where

$$\rho(\mathbf{x}) = \sum_{\alpha} n_{\alpha} |\psi_{\alpha}(\mathbf{x})|^2, \quad \rho_{\text{pol}}(\mathbf{x}) = \left\langle \frac{\delta g_0}{\delta \mu(\mathbf{x})} \right\rangle_{\text{pol}} ,$$

the relation (3.13) then translates into

$$\mathbf{D} = \mathbf{E} + 4\pi \mathbf{P} \quad (3.19)$$

and correlations, expressed in terms of the functional (3.10) or (3.11) which is obtained by the requirement (3.7), are pictured as the polarization of a polarizable "medium" built up by independent single-particle states. This polarization makes up for the difference of the electric field \mathbf{E} and the displacement \mathbf{D} which accounts for the total charge Ze in a Z -electron system. This picture leads to nontrivial relations for g_0 which we now derive.

In the equation of motion (3.4) the source of \mathbf{E} appears as (we neglect exchange for a moment)

$$\frac{1}{4\pi} \nabla \cdot \mathbf{E} = g_0(\mathbf{x}) \sum_{\alpha} n_{\alpha} |\psi_{\alpha}(\mathbf{x})|^2 ; \quad (3.20)$$

Eqs. (3.13) and (3.17) then lead to the relation

$$\begin{aligned} & [1 - g_0(\mathbf{x})] \sum_{\alpha} n_{\alpha} |\psi_{\alpha}(\mathbf{x})|^2 \\ &= \rho_{\text{pol}}(\mathbf{x}) \\ &= - \sum_{\alpha} n_{\alpha} \int d^3x' \psi_{\alpha}^{*}(\mathbf{x}') \frac{\delta g_0(\mathbf{x}')}{\delta \mu(\mathbf{x})} \mathcal{V}_{\text{pol}}(\mathbf{x}') \psi_{\alpha}(\mathbf{x}') , \end{aligned} \quad (3.21)$$

which is a functional-differential relation for the correlation functional g_0 .

To include the exchange potential, a purely quantum-mechanical effect, into this line of argumentation which is essentially classical we proceed as follows. The source of the electric field in (3.4) is the operator acting as the exchange convolution

$$\begin{aligned} & \frac{1}{4\pi} \nabla \cdot \mathbf{E}|_{\text{QM}} = \sum_{\alpha} n_{\alpha} \{g_0(\mathbf{x}) |\psi_{\alpha}(\mathbf{x})|^2 \\ & - [1 - g_0(\mathbf{x})] \psi_{\alpha}^{*}(\mathbf{x}) \psi_{\alpha}(\mathbf{x}')\} . \end{aligned} \quad (3.22)$$

We employ essentially the same idea as above if we now equate

$$\left\langle\left\langle \frac{1}{4\pi} \nabla \cdot \mathbf{E} |_{\text{QM}(\mathbf{x})} \right\rangle\right\rangle = n(\mathbf{x}), \quad (3.23)$$

where the average $\langle\langle \dots \rangle\rangle$ is obtained by calculating

$$\langle\langle \dots \rangle\rangle = \sum_{\beta} n_{\beta} \int d^3x' \psi_{\beta}^*(\mathbf{x}') \dots \psi_{\beta}(\mathbf{x}'). \quad (3.24)$$

Equation (3.23) leads to

$$[1 - g_0(\mathbf{x})] \sum_{\alpha} n_{\alpha} |\psi_{\alpha}(\mathbf{x})|^2 = \frac{Z}{Z+1} \rho_{\text{pol}}(\mathbf{x}). \quad (3.25)$$

As is clear from its derivation this relation pertains to rigid charge distributions, dynamical effects resulting from nonlinear feedback are not included.

In the context of quantum field theory which is the common background of all our discussions such effects are expressed in terms of correlation functions. (The term "correlation" is used here in a context slightly different from the one employed above; however, we do not think that this should cause any imminent confusion.) Charge density-density correlations are given by

$$\rho_n(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n) = \frac{1}{n!} \frac{\delta^n E_{\text{tot}}}{\delta\mu(\mathbf{x}_1) \delta\mu(\mathbf{x}_2) \dots \delta\mu(\mathbf{x}_n)}. \quad (3.26)$$

$$\rho_{\text{corr}}(\mathbf{x}) = \sum_{n=2} \frac{1}{n!} \int d^3x_1 \dots \int d^3x_{n-1} \left\langle \frac{\delta^n g_0}{\delta\mu(\mathbf{x}) \delta\mu(\mathbf{x}_1) \dots \delta\mu(\mathbf{x}_{n-1})} \right\rangle_{\text{pol}}, \quad (3.29)$$

where

$$\left\langle \frac{\delta^n g_0}{\delta\mu(\mathbf{x}) \dots \delta\mu(\mathbf{x}_{n-1})} \right\rangle_{\text{pol}} = \sum_{\alpha} n_{\alpha} \int d^3x' \psi_{\alpha}^*(\mathbf{x}') \frac{\delta^n g_0(\mathbf{x}')}{\delta\mu(\mathbf{x}) \dots \delta\mu(\mathbf{x}_{n-1})} \mathcal{V}_{\text{pol}}(\mathbf{x}') \psi_{\alpha}(\mathbf{x}'), \quad (3.30)$$

i.e., $\rho_{\text{corr}}(\mathbf{x})$ does not contain any MBPT loops representing quantum fluctuations although, as a closer analysis shows,

$$\bar{\rho}_n(\mathbf{x}) := \frac{1}{n!} \int d^3x_1 \dots \int d^3x_{n-1} \left\langle \frac{\delta^n g_0}{\delta\mu(\mathbf{x}) \delta\mu(\mathbf{x}_1) \dots \delta\mu(\mathbf{x}_{n-1})} \right\rangle_{\text{pol}} \quad (3.31)$$

is of n th order of the electron-electron potential $V(\mathbf{x}', \mathbf{x}'')$ [see (3.2)],

$$\bar{\rho}_n(\mathbf{x}) = O(V^n),$$

and, hence, is given by MBPT graphs with at least n loops if any but the g -Hartree, $g = g_0$, single-particle basis is used to set up the usual Goldstone graphical expansion. Employing the g -Hartree basis for $g = g_0$ determined from (3.7) lumps all these at least n th-order loop graphs into an expectation value $\bar{\rho}_n(\mathbf{x})$ of the n th-order derivative of the one functional (3.10). Therefore, we shall call, henceforth, g_0 the correlation functional: the original Hamiltonian, i.e., the Hamiltonian of nonrelativistic or relativistic quantum electrodynamics in Coulomb gauge, used to derive the equations of motion (3.4) for electrons interacting in atomic or molecular configurations contains only the Coulomb interactions of electronic charge distributions; the correlation charge thus stands for essential dynamic manifestation of the in-

teraction. It is intuitively clear that [(3.26) is symmetric in $\mathbf{x}_1, \dots, \mathbf{x}_n]$

$$\rho_{\text{corr}}(\mathbf{x}) := \sum_{n=2} \int d^2x_1 \dots \int d^3x_{n-1} \rho_n(\mathbf{x}, \mathbf{x}_1, \dots, \mathbf{x}_{n-1}) \quad (3.27)$$

represents the charge density induced by dynamic effects. The consistency condition (3.25) then becomes

$$[1 - g_0(\mathbf{x})] \sum_{\alpha} n_{\alpha} |\psi_{\alpha}(\mathbf{x})|^2 = \frac{Z}{Z+1} [\rho_{\text{pol}}(\mathbf{x}) + \rho_{\text{corr}}(\mathbf{x})], \quad (3.28)$$

and is an extension of the Clausius-Mosotti³ and Lorenz-Lorentz³ relations in the spirit of the identifications (3.17)–(3.19).

If we calculate $\rho_{\text{corr}}(\mathbf{x})$ from (3.7) and the equations of motion (3.4) we obtain the remarkable result that the correlation charge density is entirely determined by the correlation functional g_0 . More precisely speaking, calculating $\rho_{\text{corr}}(\mathbf{x})$ by performing the appropriate functional derivatives on the total energy of the atom or molecule given in terms of g -Hartree orbitals and the functional g_0 by (3.7) we find

teraction.

We end this section with an example. Let f be a real function of one real variable. We set

$$g_0 = f \left[\sum_{\alpha} n_{\alpha} |\psi_{\alpha}(\mathbf{x})|^2 \right], \quad (3.32)$$

where $\psi_{\alpha}(\mathbf{x})$ are g -Hartree orbitals calculated for $g = g_0$: (3.32) is, hence, an implicit representation for the functional g_0 which is, $\mu(\mathbf{x})$ given, also a function of \mathbf{x} . The function f might be thought of as given in terms of parameters $\gamma_0, \dots, \gamma_k$ in the discussion following (3.11). By explicit calculation we now show (see the Appendix for details) that

$$\rho_{\text{pol}}(\mathbf{x}) = \int d^3x' f' \left[\sum_{\alpha} n_{\alpha} |\psi_{\alpha}(\mathbf{x}')|^2 \right] F(\mathbf{x}', \mathbf{x}), \quad (3.33)$$

where f' denotes the derivative of f and $F(\mathbf{x}, \mathbf{x}')$ is given in terms of the electron-electron interaction (3.2) and g -Hartree single-particle orbitals and is, hence, considered

as an explicitly known function once a real function f is prescribed. Important constraints on the choice of f then follow from (3.31). We should emphasize, however, that at least one constant is not fixed: (3.31) is homogeneous in $(1-g_0)$ and, hence, an overall normalization is left undetermined. Finally, we remark that there is no total polarization and no correlation charge, i.e.,

$$\int d^3x \rho_{\text{pol}}(\mathbf{x}) = 0 \quad (3.34)$$

and

$$\int d^3x \rho_{\text{corr}}(\mathbf{x}) = 0 \quad (3.35)$$

or, even stronger,

$$\int d^3x \bar{\rho}_n(\mathbf{x}) = 0, \quad n = 1, 2, 3, \dots \quad (3.36)$$

These equations follow from relations [see (A24) and (A31)] reflecting very general properties of quantum field theory which should be traced back to gauge invariance as *prima causa*. At a less ambitious level the relations in question can be explicitly understood in MBPT.

For the choice (3.32) of the correlation functional g_0 , explicit expressions for $\bar{\rho}_n(\mathbf{x})$ in terms of the electron-electron Coulomb potential $V(\mathbf{x}', \mathbf{x}'')$ and the g -Hartree single-particle orbitals $\{\psi_\alpha(\mathbf{x})\}$ can be derived which automatically obey (A24) and (A31).

IV. CONCLUSIONS

Our goal was to establish a perturbative approach for the calculation of observables of inhomogeneous many-electron systems which incorporates an algorithm for the choice of an optimized zeroth-order approximation in the sense that higher-order perturbations converge rapidly and in a controlled manner; at the same time the scheme should be constructed such that it holds for nonrelativistic as well as relativistic systems.

The starting point of our construction was the g -Hartree mean field which contrary to other adaptations¹³ of the Hartree-Fock mean field has the advantage of being derived from a variational principle¹¹ and/or the method of stationary phases applied to the partition function of an inhomogeneous many-electron system.

The next step was to adapt the parameter g such that the total energy is exactly given by the g -Hartree energy [Eq. (3.7)], i.e., such that the sum of perturbative loop contributions vanishes. This condition yields a functional g_0 of the external nuclear Coulomb potential $\mu(\mathbf{x})$ [Eqs. (3.10) or (3.11)] which is, of course, a very complicated entity.

The correlation functional $g_0[\mu]$ not only determines the total energy, the charge density and the correlation charge are equally fixed: the given functional $g_0[\mu]$ determines a set of g -Hartree orbitals $\{\psi_\alpha(\mathbf{x})\}$ via the g -Hartree equations (3.4); the total energy, the charge density, and the correlation charge density are given as expectation values of g_0 , its first-order and higher-order derivatives, respectively, [Eqs. (3.7), (3.13), and (3.29)]; all loop contributions representing higher-order perturbative contributions vanish.

For many problems the choice of the external Coulomb potential $\mu(\mathbf{x})$ as the functional variable is a particularly convenient one. The stable configuration of Born-Oppenheimer molecules, for instance, is determined precisely as the configuration in which the first-order response to a variation in the external Coulomb potential vanishes; the second order then yields the harmonic vibrational spectrum. External fields as functional variables prove equally useful in the description of phenomena connected with atoms or molecules caught in solid-state matrices, in ionic lattices, etc.

Theoretically speaking, $\mu(\mathbf{x})$ is conjugate to the observed electron density $n(\mathbf{x})$

$$n(\mathbf{x}) = \frac{\delta E_{\text{tot}}}{\delta \mu(\mathbf{x})} \quad (4.1)$$

in the sense of a Legendre transform. Hence, our approach is dual to the energy-density functional theory developed by Hohenberg-Kohn-Sham, the g -Hartree equations playing a role remotely reminiscent to the Kohn-Sham equations. Formally, our approach has the advantage of not employing the local-density approximation (LDA) necessary to construct the inverse⁷ of (4.1) in a manner which can be exploited in practical terms. Not taking recourse to the LDA and parametrizing correlations in terms of the correlation functional $g_0[\mu]$ means that all approximation schemes invented within the scope set by g -Hartree theory retain a close connection to the original microscopic equation of motion, the many-body Schrödinger equation.

The g -Hartree correlation functional theory can be extended to encompass the description of inhomogeneous many-electron systems in thermodynamic equilibrium: let \mathcal{H} be the Hamiltonian, the grand-canonical potential

$$\begin{aligned} \mathcal{G}[\mu; \beta] &= -\beta^{-1} \ln Z, \\ Z &= \text{tr}(e^{-\beta \mathcal{H}}), \end{aligned} \quad (4.2)$$

is a functional of μ and a function of the inverse temperature β and plays now, at finite temperatures, the role of the total energy; at vanishing temperature we have

$$\mathcal{G}[\mu; \infty] = E_{\text{tot}}[\mu]. \quad (4.3)$$

The central Eq. (3.7) generalizes to

$$\mathcal{G}[\mu; \beta] = \mathcal{G}_{g-H}[\mu; \beta] \Big|_{g=g_0}, \quad (4.4)$$

where now, instead of (3.10) and (3.11),

$$g_0 = g_0[\mu; \beta] \quad (4.5)$$

or

$$g_0 = g_0[\mu; \beta](\mathbf{x}).$$

Physically speaking, this means that the grand canonical potential for an (inhomogeneous) system of interacting electrons is exactly represented (up to an obvious term representing the mean-field contribution) by an ideal gas of g -Hartree single-particle excitations.¹²

The charge density in thermal equilibrium and its correlations are again given by the functional derivatives

$$\begin{aligned}\rho_n(\mathbf{x}_1, \dots, \mathbf{x}_n) &= \frac{\delta^n \mathcal{G}[\mu; \beta]}{\delta\mu(\mathbf{x}_1) \cdots \delta\mu(\mathbf{x}_n)} \\ &= \frac{\delta^n (\mathcal{G}_{g-H}[\mu; \beta]|_{g=g_0})}{\delta\mu(\mathbf{x}_1) \cdots \delta\mu(\mathbf{x}_n)},\end{aligned}\quad (4.6)$$

and the discussion of atomic and molecular properties at finite temperatures follows the one developed above in a straightforwardly analogous manner.

It should be clear from (4.3) that our derivations above can be phrased as a thermodynamical description of an equilibrium state at zero temperature. In a subsequent publication we plan to study implications of our approach numerically and show that the speed of convergence of MBPT can be greatly improved by a judicious choice of the correlation functional g_0 .

APPENDIX

We shall discuss in this section the formal aspects of the theory developed above and derive explicitly the for-

$$\int d^3x' \psi_\beta^*(\mathbf{x}') \left[\delta(\mathbf{x} - \mathbf{x}') + \frac{\delta}{\delta\mu(\mathbf{x})} \mathcal{V}_g(\mathbf{x}') - \frac{\delta\epsilon_\alpha}{\delta\mu(\mathbf{x})} \right] \psi_\alpha(\mathbf{x}') = (\epsilon_\alpha - \epsilon_\beta) \int d^3x' \psi_\beta^*(\mathbf{x}') \frac{\delta\psi_\alpha(\mathbf{x}')}{\delta\mu(\mathbf{x})}.\quad (A2)$$

This equation contains two separate bits of information: for $\alpha \neq \beta$ we obtain an integral equation for the derivative of the orbital $\psi_\alpha(\mathbf{x}')$ with respect to the functional variable $\mu(\mathbf{x})$

$$\frac{\delta\psi_\alpha(\mathbf{x}')}{\delta\mu(\mathbf{x})} = \sum_{\gamma \neq \alpha} \frac{\psi_\gamma(\mathbf{x}')}{\epsilon_\alpha - \epsilon_\gamma} \left[\psi_\gamma^*(\mathbf{x}) \psi_\alpha(\mathbf{x}) + \int d^3x'' \psi_\gamma^*(\mathbf{x}'') \frac{\delta\mathcal{V}_g(\mathbf{x}'')}{\delta\mu(\mathbf{x})} \psi_\alpha(\mathbf{x}'') \right],\quad (A3)$$

for $\alpha = \beta$ an equation for the derivative of ϵ_α

$$\frac{\delta\epsilon_\alpha}{\delta\mu(\mathbf{x})} = |\psi_\alpha(\mathbf{x})|^2 + \int d^3x'' \psi_\alpha^*(\mathbf{x}'') \frac{\delta\mathcal{V}_g(\mathbf{x}'')}{\delta\mu(\mathbf{x})} \psi_\alpha(\mathbf{x}'').\quad (A4)$$

Although the first terms in (A3) and (A4) simply are the well-known results of first-order perturbation theory we stress that these expressions for the derivatives of ψ_α and ϵ_α contain all the information carried by the g -Hartree equations (3.4). Clearly, similar expressions for similar equations, e.g., the Hartree or Hartree-Fock equations, have been derived in the literature^{4,5} by parametrizing the general variation $\delta\mu(\mathbf{x})$ (see above) by a few physically relevant constants and thus replacing the Fréchet derivatives by partial derivatives with respect to these constants. We shall employ the general formalism of functional analysis since it allow a compact and versatile formulation of our equations.

Physically speaking the new concept is that through Eqs. (3.7) and (3.10) or (3.11) the parameter g becomes a functional g_0 accounting for *all* Coulomb correlations predicted by nonrelativistic or relativistic quantum electrodynamics; functional derivatives of g_0 will play an important role which we shall try to elucidate in the following.

Again it is clear that correlations have been taken into account in calculating first-, second-, and higher-order responses of atomic and molecular observables and that

mulas referred to in Secs. II, III, and IV. We shall do this in a way which we think is particularly suitable for a numerical evaluation. In particular we shall refrain from establishing a graphical representation of resulting integral equations and not present perturbation series in terms of Feynman graphs but rather employ finally a consequent matrix notation adapted to the use of finite basis sets approximating Hilbert spaces of physical states.

We start by differentiating the g -Hartree equation (3.4)

$$\begin{aligned}\frac{\delta}{\delta\mu(\mathbf{x})} [D + \mathcal{V}_g(\mathbf{x}') - \epsilon_\alpha] \psi_\alpha(\mathbf{x}') \\ = \left[\delta(\mathbf{x} - \mathbf{x}') + \frac{\delta}{\delta\mu(\mathbf{x})} \mathcal{V}_g(\mathbf{x}') - \frac{\delta\epsilon_\alpha}{\delta\mu(\mathbf{x})} \right] \psi_\alpha(\mathbf{x}') \\ + [D + \mathcal{V}_g(\mathbf{x}') - \epsilon_\alpha] \frac{\delta\psi_\alpha(\mathbf{x}')}{\delta\mu(\mathbf{x})} = 0.\end{aligned}\quad (A1)$$

Multiplying by $\psi_\beta^*(\mathbf{x}')$ and integrating we find

an extensive literature^{14,15} can be found on the subject. However, in introducing the functional g_0 we obtained a compact and completely general formulation of the problem of correlations in many-electron systems, which has a transparent physical interpretation and, hence, is amenable to physically motivated approximations.

We now use (A5) to derive an integral equation for the derivative of the g -Hartree potential. Taking into account the functional dependence of g_0 we have in obvious notation

$$\frac{\delta\mathcal{V}_{g_0}(\mathbf{x}')}{\delta\mu(\mathbf{x})} = \frac{\delta\mathcal{V}_g(\mathbf{x}')^{(\text{part})}}{\delta\mu(\mathbf{x})} \Big|_{g=g_0} + 2 \left\langle \frac{\delta g_0}{\delta\mu(\mathbf{x})} \right\rangle_{\text{pol}},\quad (A5)$$

where we defined [repeating (3.14) and (3.16) for the sake of clarity]

$$\left\langle \frac{\delta g_0}{\delta\mu(\mathbf{x})} \right\rangle_{\text{pol}} = \frac{1}{2} \sum_\alpha n_\alpha W_{\text{pol}\alpha}^\alpha(\mathbf{x})\quad (A6)$$

and

$$(W_{\text{pol}})_{\beta}^\alpha(\mathbf{x}) = \int d^3x' \psi_\alpha^*(\mathbf{x}') \frac{\delta g_0(\mathbf{x}')}{\delta\mu(\mathbf{x})} \mathcal{V}_{\text{pol}(\mathbf{x}')} \psi_\beta(\mathbf{x}')\quad (A7)$$

with

$$\begin{aligned}\mathcal{V}_{\text{pol}(\mathbf{x}')} = \int d^3x'' V(\mathbf{x}', \mathbf{x}'') \sum_\alpha n_\alpha [|\psi_\alpha(\mathbf{x}'')|^2 \\ + \psi_\alpha^*(\mathbf{x}'') \psi_\alpha(\mathbf{x}')^*];\end{aligned}\quad (A8)$$

on the other hand, we find from the definition of \mathcal{V}_g

$$\frac{\delta \mathcal{V}_g(\mathbf{x}')^{(\text{part})}}{\delta \mu(\mathbf{x})} = \sum_{\beta} n_{\beta} \int d^3 x'' V(\mathbf{x}', \mathbf{x}'') \left[g \left[\psi_{\beta}^*(\mathbf{x}'') \frac{\delta \psi_{\beta}(\mathbf{x}'')}{\delta \mu(\mathbf{x})} + \frac{\delta \psi_{\beta}^*(\mathbf{x}'')}{\delta \mu(\mathbf{x})} \psi_{\beta}(\mathbf{x}'') \right] - (1-g) \left[\psi_{\beta}^*(\mathbf{x}'') \frac{\delta \psi_{\beta}(\mathbf{x}')}{\delta \mu(\mathbf{x})} + \frac{\delta \psi_{\beta}^*(\mathbf{x}'')}{\delta \mu(\mathbf{x})} \psi_{\beta}(\mathbf{x}') \right] \right] . \quad (\text{A9})$$

Inserting (A3) the desired integral equation obtains. In order to write this equation in a manner which does not obscure its simple structure by a bulky notation and, at the same time, to cast it in a form suitable for numerical analysis we employ matrix notation and introduce the following quantities.

(i) The potential matrix is

$$\begin{aligned} \mathcal{W}_{\rho}^{\rho'}(\mathbf{x}; g) &:= \sum_{\beta \neq \gamma} \frac{n_{\beta} - n_{\gamma}}{\varepsilon_{\beta} - \varepsilon_{\gamma}} [gV - (1-g)\bar{V}]_{\rho\gamma}^{\rho'\beta} \psi_{\gamma}^*(\mathbf{x}) \psi_{\beta}(\mathbf{x}) \\ &=: \sum_{\beta, \gamma} \bar{W}_{\rho\gamma}^{\rho'\gamma} \psi_{\gamma}^*(\mathbf{x}) \psi_{\beta}(\mathbf{x}) \end{aligned} \quad (\text{A10})$$

with

$$\bar{W}_{\rho\alpha}^{\rho'\alpha} = 0 \quad \text{for all } \alpha ,$$

$$\begin{aligned} V_{\rho\gamma}^{\rho'\beta} &= \int d^3 x' \int d^3 x'' \psi_{\rho'}^*(\mathbf{x}') \psi_{\beta}^*(\mathbf{x}'') \\ &\quad \times V(\mathbf{x}', \mathbf{x}'') \psi_{\rho}(\mathbf{x}') \psi_{\gamma}(\mathbf{x}'') , \end{aligned}$$

$$\bar{V}_{\rho\gamma}^{\rho'\beta} = V_{\gamma\rho}^{\rho'\beta} .$$

(ii) Derivatives of the g -Hartree potential in matrix form

$$\mathcal{A}_{\rho}^{\rho'}(\mathbf{x}; g) := \int d^3 x' \psi_{\rho'}^*(\mathbf{x}') \frac{\delta \mathcal{V}_g(\mathbf{x}')}{\delta \mu(\mathbf{x})} \psi_{\rho}(\mathbf{x}') , \quad (\text{A11})$$

$$\mathcal{A}_{\rho}^{\rho'}(\mathbf{x}'; g)^{(\text{part})} := \int d^3 x' \psi_{\rho'}^*(\mathbf{x}') \frac{\delta \mathcal{V}_g(\mathbf{x}')^{(\text{part})}}{\delta \mu(\mathbf{x})} \psi_{\rho}(\mathbf{x}') . \quad (\text{A12})$$

$$\begin{aligned} n(\mathbf{x}) &= \frac{\delta E_{\text{tot}}}{\delta \mu(\mathbf{x})} \\ &= \frac{\delta}{\delta \mu(\mathbf{x})} \left[\sum_{\alpha} n_{\alpha} \left[\varepsilon_{\alpha} - \frac{1}{2} \int d^3 x' \psi_{\alpha}^*(\mathbf{x}') \mathcal{V}_{g_0}(\mathbf{x}') \psi_{\alpha}(\mathbf{x}') \right] \right] , \end{aligned} \quad (\text{A16})$$

(A4) and (A5) then lead to

$$\begin{aligned} n(\mathbf{x}) &= \sum_{\alpha} n_{\alpha} |\psi_{\alpha}(\mathbf{x})|^2 + \sum_{\alpha} n_{\alpha} \int d^3 x' \psi_{\alpha}^*(\mathbf{x}') \frac{\delta \mathcal{V}_{g_0}(\mathbf{x}')^{(\text{part})}}{\delta \mu(\mathbf{x})} \psi_{\alpha}(\mathbf{x}') + 2 \left\langle \frac{\delta g_0}{\delta \mu(\mathbf{x})} \right\rangle_{\text{pol}} \\ &\quad - 2 \frac{1}{2} \int d^3 x' \sum_{\alpha} n_{\alpha} \psi_{\alpha}^*(\mathbf{x}') \frac{\delta \mathcal{V}_{g_0}(\mathbf{x}')^{(\text{part})}}{\delta \mu(\mathbf{x})} \psi_{\alpha}(\mathbf{x}') - \left\langle \frac{\delta g_0}{\delta \mu(\mathbf{x})} \right\rangle_{\text{pol}} \\ &= \sum_{\alpha} n_{\alpha} |\psi_{\alpha}(\mathbf{x})|^2 + \left\langle \frac{\delta g_0}{\delta \mu(\mathbf{x})} \right\rangle_{\text{pol}} . \end{aligned} \quad (\text{A17})$$

The second derivative of E_{tot} is easily cast in the form

$$\frac{\delta^2 E_{\text{tot}}}{\delta \mu(\mathbf{x}_1) \delta \mu(\mathbf{x}_2)} = \frac{\delta \sum_{\alpha} n_{\alpha} |\psi_{\alpha}(\mathbf{x}_2)|^2}{\delta \mu(\mathbf{x}_1)} + \left\langle \frac{\delta^2 g_0}{\delta \mu(\mathbf{x}_1) \delta \mu(\mathbf{x}_2)} \right\rangle_{\text{pol}} + \sum_{\alpha} n_{\alpha} \int d^3 x' \psi_{\alpha}^*(\mathbf{x}') \frac{\delta g_0(\mathbf{x}')}{\delta \mu(\mathbf{x}_2)} \frac{\delta \mathcal{V}_{\text{pol}}(\mathbf{x}')}{\delta \mu(\mathbf{x}_1)} \psi_{\alpha}(\mathbf{x}') . \quad (\text{A18})$$

Both quantities are obviously related by

$$\mathcal{A}_{\rho}^{\rho'}(\mathbf{x}; g_0) = \mathcal{A}_{\rho}^{\rho'}(\mathbf{x}; g_0)^{(\text{part})} + (W_{\text{pol}})_{\rho}^{\rho'}(\mathbf{x}) . \quad (\text{A13})$$

This integral equation implicitly given by (A5), (A9), and (A3) then reads

$$\mathcal{A}_{\rho}^{\rho'}(\mathbf{x}; g_0) = \mathcal{W}_{\rho}^{\rho'}(\mathbf{x}; g_0) + (W_{\text{pol}})_{\rho}^{\rho'}(\mathbf{x}) + \bar{\mathcal{W}}_{\rho\gamma}^{\rho'\beta} \mathcal{A}_{\beta}^{\gamma}(\mathbf{x}; g_0) ; \quad (\text{A14})$$

it admits a unique solution

$$\mathcal{A}_{\rho}^{\rho'}(\mathbf{x}; g_0) = (1 - \bar{\mathcal{W}})^{-1} |_{\rho\gamma}^{\rho'\beta} [\mathcal{W}_{\beta}^{\gamma}(\mathbf{x}; g_0) + (W_{\text{pol}})_{\beta}^{\gamma}(\mathbf{x})] \quad (\text{A15})$$

as long as $\det(1 - \bar{\mathcal{W}}) \neq 0$. It should be pointed out that the potential matrix $\bar{\mathcal{W}}$ contains the factor

$$\frac{n_{\beta} - n_{\gamma}}{\varepsilon_{\beta} - \varepsilon_{\gamma}}$$

(typical for first-order contributions) which is symmetric in the indices β, γ thus guaranteeing the hermiticity of \mathcal{W} and which, due to the factor $(n_{\beta} - n_{\gamma})$, selects transitions (occupied orbitals \rightleftharpoons virtual orbitals) as should be expected from the Pauli principle.

We are now in the position to calculate the physical charge density and charge density-density correlations. Equations (2.6) and (3.7) yield

Clearly, this expression must be symmetric under the exchange $\mathbf{x}_1 \leftrightarrow \mathbf{x}_2$; Frechét derivatives commute under very general conditions. To analyze the consequences of this symmetry we cast (A18) in a more explicit form. Analogous to (A10) and (A11) we define

$$\mathcal{U}_\rho^{\rho'}(\mathbf{x}_1, \mathbf{x}_2; g_0) := \sum_{\beta, \gamma} \frac{n_\beta - n_\gamma}{\varepsilon_\beta - \varepsilon_\gamma} \{ U + \tilde{U} \}_{\rho\gamma}^{\rho'\beta} \psi_\gamma^*(\mathbf{x}_1) \psi_\beta(\mathbf{x}_1) =: \sum_{\text{beta}, \gamma'} \bar{\mathcal{U}}_{\rho\gamma'}^{\rho'\beta}(\mathbf{x}_2) \psi_\gamma^*(\mathbf{x}_1) \psi_\beta(\mathbf{x}_1), \quad (\text{A19})$$

where

$$\begin{aligned} U_{\rho\gamma}^{\rho'\beta}(\mathbf{x}_2) &= \int d^3x' \int d^3x'' \frac{\delta g_0(\mathbf{x}')}{\delta \mu(\mathbf{x}_2)} \psi_{\rho'}^*(\mathbf{x}') \psi_\beta^*(\mathbf{x}'') V(\mathbf{x}', \mathbf{x}'') \psi_\rho(\mathbf{x}') \psi_\gamma(\mathbf{x}''), \\ \tilde{U}_{\rho\gamma}^{\rho'\beta}(\mathbf{x}_2) &= U_{\gamma\rho}^{\rho'\beta}(\mathbf{x}_2), \\ \mathcal{H}_\rho^{\rho'}(\mathbf{x}_1, \mathbf{x}_2; g_0) &:= \int d^3x' \psi_{\rho'}^*(\mathbf{x}') \frac{\delta g_0(\mathbf{x}')}{\delta \mu(\mathbf{x}_1)} \frac{\delta \mathcal{V}_g(\mathbf{x}')}{\delta \mu(\mathbf{x}_2)} \psi_\rho(\mathbf{x}'). \end{aligned} \quad (\text{A20})$$

A derivation very similar to the one which led to (A14) now yields

$$\mathcal{H}_\rho^{\rho'}(\mathbf{x}_1, \mathbf{x}_2; g_0) = \mathcal{U}_\rho^{\rho'}(\mathbf{x}_1, \mathbf{x}_2; g_0) + \bar{\mathcal{U}}_{\rho\gamma}^{\rho'\beta}(\mathbf{x}_2) \mathcal{A}_\beta^\gamma(\mathbf{x}_1; g_0). \quad (\text{A21})$$

Using

$$\frac{\delta \sum_\alpha n_\alpha |\psi_\alpha(\mathbf{x}_2)|^2}{\delta \mu(\mathbf{x}_1)} = \sum_{\beta, \gamma} \frac{n_\beta - n_\gamma}{\varepsilon_\beta - \varepsilon_\gamma} \psi_\beta^*(\mathbf{x}_2) [\psi_\beta(\mathbf{x}_1) \psi_\gamma^*(\mathbf{x}_1) + \mathcal{A}_\beta^\gamma(\mathbf{x}_1; g_0)] \psi_\gamma(\mathbf{x}_2), \quad (\text{A22})$$

which immediately derives from (A3) we get

$$\begin{aligned} \frac{\delta^2 E_{\text{tot}}}{\delta \mu(\mathbf{x}_1) \delta \mu(\mathbf{x}_2)} &= \sum_{\beta, \gamma} \frac{n_\beta - n_\gamma}{\varepsilon_\beta - \varepsilon_\gamma} \psi_\beta^*(\mathbf{x}_2) [\psi_\beta(\mathbf{x}_1) \psi_\gamma^*(\mathbf{x}_1) + \mathcal{A}_\beta^\gamma(\mathbf{x}_1; g_0)] \psi_\gamma(\mathbf{x}_2) \\ &\quad + \sum_{\alpha, \beta, \gamma} n_\alpha [\mathcal{U}_\alpha^{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2; g_0) + \bar{\mathcal{U}}_{\alpha\gamma}^{\alpha\beta}(\mathbf{x}_2) \mathcal{A}_\beta^\gamma(\mathbf{x}_1; g_0)] + \left\langle \frac{\delta^2 g_0}{\delta \mu(\mathbf{x}_1) \delta \mu(\mathbf{x}_2)} \right\rangle_{\text{pol}}. \end{aligned} \quad (\text{A23})$$

In general, this expression is not symmetric; further structural elements implied by local quantum field theory must be introduced in order to guarantee symmetry of charge density-density correlations. The matrix $W_{\text{pol}\beta}^{\alpha}(\mathbf{x})$ representing electron-electron correlations is thus endowed with a hidden index structure

$$(W_{\text{pol}})_{\beta}^{\alpha}(\mathbf{x}) = \sum_{\gamma \neq \beta} \frac{n_\gamma - n_\delta}{\varepsilon_\gamma - \varepsilon_\delta} W_{\beta\delta}^{\alpha\gamma} \psi_\gamma^*(\mathbf{x}) \psi_\delta(\mathbf{x}), \quad (\text{A24})$$

the matrix $W_{\beta\delta}^{\alpha\gamma}$ has the same symmetry and reality properties as the matrices defined in (A10). It can be shown in any order of perturbation theory that $(W_{\text{pol}})_{\beta}^{\alpha}(\mathbf{x})$ does indeed have the form (A24), a more detailed analysis in the framework of nonrelativistic or relativistic renormalized MBPT is, however, beyond the scope of this paper. Inserting now the explicit solution (A15) the symmetry of (A23) is immediately inferred from the symmetry and reality properties of $W_{\rho\gamma}^{\rho'\beta}$ and $W_{\rho\gamma}^{\rho'\beta}$.

Equation (A24) implies that

$$\int d^3x (W_{\text{pol}})_{\beta}^{\alpha}(\mathbf{x}) = 0,$$

and hence,

$$\begin{aligned} \frac{\delta g_0}{\delta \mu(\mathbf{x}_1)} &= f' \left[\sum_\alpha n_\alpha |\psi_\alpha(\mathbf{x})|^2 \right] \frac{\delta \sum_\alpha n_\alpha |\psi_\alpha(\mathbf{x})|^2}{\delta \mu(\mathbf{x}_1)} \\ &= f' \left[\sum_\alpha n_\alpha |\psi_\alpha(\mathbf{x})|^2 \right] \sum_{\beta, \gamma} \frac{n_\beta - n_\gamma}{\varepsilon_\beta - \varepsilon_\gamma} \psi_\beta^*(\mathbf{x}) [\psi_\beta(\mathbf{x}_1) \psi_\gamma^*(\mathbf{x}_1) + \mathcal{A}_\beta^\gamma(\mathbf{x}_1; g_0)] \psi_\gamma(\mathbf{x}). \end{aligned} \quad (\text{A27})$$

$$\int d^3x \left\langle \frac{\delta g_0}{\delta \mu(\mathbf{x})} \right\rangle_{\text{pol}} = 0; \quad (\text{A25})$$

there is no polarization charge. Now using (A23) to compute the correlation charge in second order

$$\rho_{\text{corr}}^{(2)}(\mathbf{x}_2) = \frac{1}{2} \int d^3x_1 \frac{\delta^2 E_{\text{tot}}}{\delta \mu(\mathbf{x}_1) \delta \mu(\mathbf{x}_2)},$$

we find

$$\rho_{\text{corr}}^{(2)}(\mathbf{x}_2) = \frac{1}{2} \int d^3x_1 \left\langle \frac{\delta^2 g_0}{\delta \mu(\mathbf{x}_1) \delta \mu(\mathbf{x}_2)} \right\rangle_{\text{pol}}; \quad (\text{A26})$$

the first term in (A23) vanishes by orthogonality of the orbitals ψ_β and ψ_δ , the terms containing $\mathcal{A}_\beta^\gamma(\mathbf{x}_2; g_0)$ do not contribute because of the same reason and so does the term $\mathcal{U}_\alpha^{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2; g_0)$ as can be read off the solution (A15) for $\mathcal{A}_\beta^\gamma(\mathbf{x}_1; g_0)$ and the definition (A19). Higher derivatives can be analyzed in the same manner and Eq. (3.30) is thus proved.

Finally, we turn to the ansatz (3.32) for the functional g_0 and compute

We then construct $(W_{\text{pol}})_{\beta}^{\alpha}(\mathbf{x}_1)$ [see (A7)] and obtain

$$(W_{\text{pol}})_{\beta}^{\alpha}(\mathbf{x}_1) = \sum_{\delta, \gamma} \bar{A}_{\beta\gamma}^{\alpha\delta} [\psi_{\gamma}^*(\mathbf{x}_1)\psi_{\delta}(\mathbf{x}_1) + \mathcal{A}_{\delta}^{\gamma}(\mathbf{x}_1; \mathbf{g}_0)] , \quad (\text{A28})$$

where $A_{\beta\gamma}^{\alpha\delta}$ follows from (A27)

$$\bar{A}_{\beta\gamma}^{\alpha\delta} = \frac{n_{\delta} - n_{\gamma}}{\varepsilon_{\delta} - \varepsilon_{\gamma}} \int d^3\mathbf{x} \psi_{\alpha}^*(\mathbf{x})\psi_{\delta}^*(\mathbf{x})f' \left[\sum_{\sigma} n_{\sigma} |\psi_{\sigma}(\mathbf{x})|^2 \right] \mathcal{V}_{\text{pol}}(\mathbf{x})\psi_{\beta}(\mathbf{x})\psi_{\gamma}(\mathbf{x}) . \quad (\text{A29})$$

Inserting (A15) and solving for $(W_{\text{pol}})_{\beta}^{\alpha}(\mathbf{x}_1)$ we arrive at

$$(W_{\text{pol}})_{\beta}^{\alpha}(\mathbf{x}_1) = \left[1 - \bar{A} \frac{1}{1 - \bar{\mathcal{W}}} \right]^{-1} \bar{A}_{\beta\gamma}^{\alpha\delta} [\psi_{\gamma}^*(\mathbf{x}_1)\psi_{\delta}(\mathbf{x}_1) + (1 - \bar{\mathcal{W}})^{-1} \mathcal{W}_{\delta}^{\gamma}(\mathbf{x}_1)] . \quad (\text{A30})$$

This solution leads to an explicit expression for the polarization density [see (A6) and (A7)] in terms of the electron-electron potential $V(\mathbf{x}, \mathbf{x}')$ [see (3.2)] and the g -Hartree single-particle orbitals symbolically written in (3.33). From (A10) the reader will immediately recognize that $(W_{\text{pol}})_{\beta}^{\alpha}(\mathbf{x}_1)$ derived from the ansatz (3.32) without

any further assumptions [apart from the merely technical ones that $\det(1 - \bar{\mathcal{W}}) \neq 0$ and $\det(1 - A - \mathcal{W}) \neq 0$] has the required form (A24).

As far as higher derivatives are concerned this relation generalizes to

$$\int d^3\mathbf{x}' \psi_{\alpha}^*(\mathbf{x}') \frac{\delta g_0(\mathbf{x}')}{\delta \mu(\mathbf{x}_1) \cdots \delta \mu(\mathbf{x}_n)} \mathcal{V}_{\text{pol}}(\mathbf{x}') \psi_{\beta}(\mathbf{x}') = \sum_{\substack{\delta_1 \cdots \delta_n \\ \gamma_1 \cdots \gamma_n}} A_{n\beta\gamma_1 \cdots \gamma_n}^{\alpha\delta_1 \cdots \delta_n} \psi_{\gamma_1}^*(\mathbf{x}_1)\psi_{\delta_1}(\mathbf{x}_1) \cdots \psi_{\gamma_n}^*(\mathbf{x}_n)\psi_{\delta_n}(\mathbf{x}_n) \quad (\text{A31})$$

which implies that the total correlation charge vanishes

$$\int d^3\mathbf{x}_1 \rho_{\text{corr}}(\mathbf{x}_1) = \sum_{n=2} \frac{1}{n!} \int d^3\mathbf{x}_1 \cdots \int d^3\mathbf{x}_n \sum_{\alpha} n_{\alpha} \int d^3\mathbf{x}' \psi_{\alpha}^*(\mathbf{x}') \frac{\delta g_0(\mathbf{x}')}{\delta \mu(\mathbf{x}_1) \cdots \delta \mu(\mathbf{x}_n)} \mathcal{V}_{\text{pol}}(\mathbf{x}') \psi_{\alpha}(\mathbf{x}') = 0 . \quad (\text{A32})$$

This is because

$$A_{n\beta\gamma_1 \cdots \gamma_n}^{\alpha\delta_1 \cdots \delta_n} = 0 \quad (\text{A33})$$

if

$$\delta_k = \gamma_k \quad \text{for all } k = 1, \dots, n .$$

Furthermore, we have

$$A_{n\beta \cdots \gamma_i \cdots \gamma_k \cdots}^{\alpha \cdots \delta_i \cdots \delta_k \cdots} = A_{n\beta \cdots \gamma_k \cdots \gamma_i \cdots}^{\alpha \cdots \delta_k \cdots \delta_i \cdots} \quad (\text{A34})$$

and obvious symmetry properties guaranteeing reality of the correlation functions.

¹For a review see, e.g., *Methods of Electronic Structure Theory*, edited by H. F. Schaefer III (Plenum, New York, 1977).

²For a review see, e.g., S. Lundquist and H. March, *Theory of the Inhomogeneous Electron Gas* (Plenum, New York, 1983); M. Levy, in *Perspectives in Quantum Chemistry*, edited by J. Jortner and B. Pullman (Kluwer Academic Editors, Dordrecht, 1989).

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