LETTER TO THE EDITOR

Static density–density correlation function for interacting ground states with ensemble v-representable number densities

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Abstract.   We consider the zero-temperature static density–density correlation function $\chi(r, r')$ corresponding to ground states (GSs) of arbitrary interacting systems, as opposed to those corresponding to systems with pure-state non-interacting v-representable GS number densities. The extended formalism involves some strict non-perturbative contributions which are not accounted for by the conventional linear-response theory. The approach therefore proves useful in addressing problems related to properties of ground and excited states of correlated systems.

The number density (ND) $n(r)$ corresponding to the ground state (GS) of an interacting system (which we for simplicity, but without loss of generality, assume to be a system of spinless fermions) corresponds to an external potential $v(r)$ and thus is referred to as *interacting v-representable* (v-rep). The change in this ND brought about by a static and local external potential, which we denote by $\delta v(r)$, is described, to linear order in $\delta v(r)$, by the static density–density correlation function $\chi(r, r')$. We have

$$\chi(r, r') := \frac{\delta n(r)}{\delta v(r')}. \tag{1}$$

Since $n(r)$ is the central quantity of the GS density-functional theory (DFT) (Hohenberg and Kohn (1964); for a comprehensive review see Dreizler and Gross (1990)), it is most natural that one calculates χ within this framework. In practical applications of the DFT, the formalism due to Kohn and Sham (1965) (KS) is of fundamental importance. In the original KS formalism, the GS functional $F[n] := E_v[n] - \int \mathrm{d}^3 r \; v(r)n(r)$, which does not explicitly depend on v (in contrast to the GS total-energy functional $E_v[n]$), is decomposed as $T_s[n] + E_H[n] + E_{xc}[n]$, where $T_s[n]$ stands for the kinetic-energy functional of a fictitious 'non-interacting' system, the KS system, $E_H[n]$ for the electrostatic Hartree energy and $E_{xc}[n]$ for the exchange–correlation energy functional defined as the difference between $F[n]$ and $T_s[n] + E_H[n]$. The minimization of the energy functional is then reduced to the self-consistent solution of a one-particle Schrödinger-type equation, the KS (1965) equation (we use the Hartree atomic units):

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}(r; [n]) \right]\psi_i(r) = \varepsilon_i \psi_i(r) \qquad (\varepsilon_i \leqslant \varepsilon_{i+1}). \tag{2}$$

This equation is arrived at through substituting in the Euler–Lagrange equation $\delta E_v[n]/\delta n(r) = \mu$ the above-indicated decomposed expression for $E_v[n]$, leading to $\delta T_s[n]/\delta n(r) + v_{eff}(r; [n]) = \mu$; the constant μ, a Lagrange multiplier, is determined by the requirement that the solution $n(r)$ of the Euler–Lagrange equation satisfy $\int \mathrm{d}^3 r \; n(r) = N$,

with N denoting the number of electrons in the system. Here, as in equation (2), $v_{eff}(\boldsymbol{r}; [n]) := v(\boldsymbol{r}) + \delta\{E_H[n] + E_{xc}[n]\}/\delta n(\boldsymbol{r}) \equiv v(\boldsymbol{r}) + v_H(\boldsymbol{r}; [n]) + v_{xc}(\boldsymbol{r}; [n])$ in which the Hartree and the exchange–correlation potential, v_H and v_{xc} respectively, correspond in an obvious way to $E_H[n]$ and $E_{xc}[n]$. KS (1965) have thus transformed the problem of determining $n(\boldsymbol{r})$ corresponding to an interacting system to one of a 'non-interacting' system:

$$n(\boldsymbol{r}) = \sum_{i=1}^{N} |\psi_i(\boldsymbol{r})|^2 \tag{3}$$

where the ψ_is are normalized eigenfunctions of equation (2). Recall that the self-consistent solution of equations (2) and (3) *by construction* yields the solution $n(\boldsymbol{r})$ of the Euler–Lagrange equation (see further on, however) so that this $n(\boldsymbol{r})$ must be identical with the ND pertaining to the GS of the *interacting* system.

As should be evident, the validity of the formalism which we have briefly described above crucially depends on the assumption concerning the existence of the functional derivative of $T_s[n]$ with respect to n in a neighbourhood of $n(\boldsymbol{r})$.

A ND describable as in equation (3) is referred to as *pure-state non-interacting v-rep*, 'pure state' signifying the fact that $n(\boldsymbol{r})$ corresponds to a single anti-symmetric N-particle wavefunction; 'non-interacting v-rep' indicating that this pure state (i.e. wavefunction) is an eigenstate of a 'non-interacting' Hamiltonian, i.e. it is a single Slater determinant. Thus the question as to whether $\delta T_s[n]/\delta n(\boldsymbol{r})$ exists in some neighbourhood of $n(\boldsymbol{r})$ is equivalent to that of whether the function $n(\boldsymbol{r})$ under consideration is pure-state non-interacting v-rep (see, e.g., Dreizler and Gross (1990), p 49). The fact that there exist NDs, i.e. non-negative and normalized-to-N functions of $\boldsymbol{r}$ (possibly extended by the requirement of once-differentiability to guarantee a finite kinetic energy (Gilbert (1975), Lieb (1982); see $\mathcal{I}_N$ defined below)), which are not pure-state non-interacting v-rep (Englisch and Englisch 1983) implies that in general $T_s[n]$ is not a differentiable functional of n.

The kinetic-energy functional due to Lieb (1982, 1983)

$$T_L[n] := \inf_{\widehat{D}\to n} \mathrm{tr}\{\widehat{D}\widehat{T}\} \tag{4}$$

defined, for three-dimensional systems, on the set $\mathcal{I}_N := \{n|n(\boldsymbol{r}) \geqslant 0, n^{1/2}(\boldsymbol{r}), \boldsymbol{\nabla} n^{1/2}(\boldsymbol{r}) \in L^2, \int \mathrm{d}^3r\, n(\boldsymbol{r}) = N\}$, has been shown (Englisch and Englisch 1983, 1984a, b) to be differentiable on the set of *ensemble v-rep* NDs (i.e. all *physical* NDs) and nowhere else. In equation (4), $\widehat{D}$ stands for the density operator, defined in terms of a complete set of orthonormal anti-symmetric N-particle states $\{|\Psi_s\rangle\}$: $\widehat{D} := \sum_s d_s |\Psi_s\rangle\langle\Psi_s|$, where $d_s \geqslant 0$ and $\sum_s d_s = 1$. With

$$F_L[n] := \inf_{\widehat{D}\to n} \mathrm{tr}\{\widehat{D}(\widehat{T} + \widehat{V})\} \tag{5}$$

the counterpart of $F[n]$ introduced above, where $\widehat{V}$ stands for the interaction part of the total Hamiltonian, the exchange–correlation energy functional is defined through the same formal expression as that involving $F[n]$ and $T_s[n]$ with these replaced by $F_L[n]$ and $T_L[n]$ respectively. Thus the KS equation corresponding to this $E_{xc}[n]$ retains the form presented in equation (2), with the difference that v_{xc} is now defined as the first functional derivative of Lieb's $E_{xc}[n]$. The expression for the ND in equation (3), on the other hand, has to be changed into

$$n(\boldsymbol{r}) = \sum_{i=1}^{\infty} f_i |\psi_i(\boldsymbol{r})|^2 \tag{6}$$

where the 'occupation numbers' f_i must satisfy the following constraints: $f_i = 1$ for $\varepsilon_i < \mu$; $f_i = 0$ for $\varepsilon_i > \mu$; $0 \leqslant f_i \leqslant 1$ for $\varepsilon_i = \mu$; and $\sum_{i=1}^{\infty} f_i = N$. These occupation numbers have to be obtained self-consistently and μ coincides with the eigenenergy of the multiplet of the highest occupied (degenerate) eigenfunctions of equation (2)†. A natural consequence of the restrictions imposed upon the f_is is that $\sum_{i;\varepsilon_i=\mu} f_i = M$, an integer, satisfying $0 \leqslant M \leqslant g_\mu$ where $g_\mu := \sum_{i;\varepsilon_i=\mu} 1$. We adopt the following conventions: when ψ_N is non-degenerate (recall that we number the states according to $\varepsilon_i \leqslant \varepsilon_{i+1}$), $\varepsilon_N < \mu < \varepsilon_{N+1}$ and $M = 0$; when, on the other hand, ψ_N is degenerate, $\mu = \varepsilon_{N-M+1} = \cdots = \varepsilon_{N-M+g_\mu}$ and $M \geqslant 1$. Clearly, $g_\mu \geqslant M$ and when $g_\mu > M$, some of the f_is (at least two) satisfy $0 \leqslant f_i < 1$. The above conventions imply that $M = 0$ and $g_\mu = 0$ are equivalent. Note in passing that by considering the GS total-energy functional $E_v[n]$ as a functional of v, denoted by $E[v]$ (explicitly, $E[v] := \inf_{n \in \mathcal{I}_N}\{F_L[n] + \int \mathrm{d}^3 r \ v(r)n(r)\}$), we have $n(r) = \delta E[v]/\delta v(r)$, for $F_L[n] \equiv \sup_{v \in \mathcal{V}}\{E[v] - \int \mathrm{d}^3 r \ v(r)n(r)\}$, with $\mathcal{V}$ denoting the set of all *local* potentials pertaining to $L^{3/2} + L^{\infty}$ ($v \in L^{3/2} + L^{\infty} \iff v = v_{3/2} + v_{\infty}$, with $v_{3/2} \in L^{3/2}$, i.e. $\{\int \mathrm{d}^3 r \ |v_{3/2}(r)|^{3/2}\}^{2/3} < \infty$, and $|v_{\infty}|$ a bounded function), is the Legendre transform of $E[v]$ (Lieb 1982, 1983). From this and equation (1) it follows that $\chi(r, r') \equiv \delta^2 E[v]/(\delta v(r) \delta v(r'))$ and hence that $\chi(r, r') \equiv \chi(r', r)$.

As mentioned above, it is most natural to evaluate $\chi(r, r')$ within the (generalized) KS formalism. To this end one changes v into $v + \delta v$ and evaluates the corresponding self-consistent ND, to be denoted by $n + \delta n$; this density pertains to the perturbed *interacting* system. At self-consistency the effective potential in equation (2) has the form $v_{eff}(r; [n + \delta n])$ which by first-order functional expansion around n can be written as

$$v_{eff}(r; [n]) + \int \mathrm{d}^3 r' \ C(r, r') \delta n(r')$$

where

$$C(r, r') := \left.\frac{\delta(v_H(r; [n']) + v_{xc}(r; [n']))}{\delta n'(r')}\right|_{n'=n} \equiv \left.\frac{\delta^2(E_H[n'] + E_{xc}[n'])}{\delta n'(r)\, \delta n'(r')}\right|_{n'=n}$$
$$\equiv v_c(r - r') + K_{xc}(r, r') \tag{7}$$

with $v_c(r - r')$ the two-particle (e.g. Coulomb) interaction function and $K_{xc}(r, r') := \delta v_{xc}(r; [n'])/\delta n'(r')|_{n'=n}$ (since both C and K_{xc} are second functional derivatives with respect to n', we have $C(r, r') = C(r', r)$ and $K_{xc}(r, r') = K_{xc}(r', r)$); the above $C \delta n$ in $v_{eff} + C \delta n$ can be merged with δv and thus δn can be viewed as the change in the density of the non-interacting KS system brought about by the change in the effective potential $v_{eff}[n]$, i.e. $\delta v_{eff}[n]$, equal to $\delta v' := \delta v + C \delta n$. Consequently, by linear-response theory we have $\delta n = \chi_0 \delta v' \equiv \chi_0 \delta v + \chi_0 C \delta n$, or equivalently

$$\delta n = (I - \chi_0 C)^{-1} \chi_0 \delta v. \tag{8}$$

Here χ_0 stands for the density–density correlation function of the non-interacting KS system,

$$\chi_0(r, r') := \frac{\delta n(r)}{\delta v_{eff}(r'; [n])}. \tag{9}$$

By comparing equation (8) with equation (1) it follows that

$$\chi = (I - \chi_0 C)^{-1} \chi_0 \iff \chi = \chi_0 + \chi_0 C \chi. \tag{10}$$

The second of these equations is of the Dyson type, the interaction effects neglected in χ_0 being accounted for by a two-point correlation function, C. Under the assumption that the

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† Throughout we ascribe 'degeneracy' both to eigenfunctions (somewhat in violation of purists' usage) and eigenvalues.

explicit functional form of $v_{xc}[n]$ is known (as is the case for instance within the commonly used local-density approximation (LDA) (Kohn and Sham 1965)), evaluation of $K_{xc}[n]$ and thus of $C[n]$ is straightforward. We note that since both C and χ are symmetric (see the text following equation (7) and that following equation (6)), from $\chi_0 = \chi(I + C\chi)^{-1}$, which is obtained from equation (10), it is seen that similarly $\chi_0(r, r') = \chi_0(r', r)$.

In what follows we give our full attention to the explicit evaluation of χ_0. To our knowledge no treatment of χ_0 corresponding to systems with ensemble v-rep ND (as exemplified by the right-hand side of equation (6)) is available in the literature. As we shall see, the χ_0 pertaining to such systems strongly depends on the nature of the perturbing potential. This is in contrast with the commonly held view that, within the linear-response theory, the response functions are independent of the perturbations.

In obtaining the static χ_0, following the definition in equation (9), we need to calculate variations in $n(r)$ to *linear* order in δv, and thus variations in both ψ_is and f_is to linear order in δv (in what follows we denote the *linear* variations by δ_1). It is in particular considerations with regard to variations in f_is that make determination of χ_0 non-trivial. An f_i can vary in two ways, stepwise or smoothly. The former type of variation *cannot* be dealt with by perturbation theory, or any theory based on the assumption of an analytic connection between δv and δf_i. This stepwise variation in f_i is a consequence of the strict constraints imposed upon the 'occupation' numbers: f_i can deviate from zero and unity if it corresponds to the highest occupied multiplet of degenerate KS eigenstates. Thus *any* perturbation δv, no matter how weak, that removes a degeneracy at μ in *any* arbitrary order of the perturbation theory, gives rise to a *jump* (towards 0 or 1) in some f_i (or f_is). The second type of variation that an f_i can undergo is a continuous variation which concerns only the f_is which pertain to those degenerate states at μ that remain degenerate to *all* orders of the perturbation theory ('exact' degeneracies). Generally, such degeneracies occur when the symmetry group of the perturbation δv coincides with that of the external potential v. However (Messiah 1975), even for perturbations δv whose symmetry groups are proper subgroups of the symmetry group of v, certain of the degeneracies can be exact (the 'Stark effect').

The only general and practical way for separating 'exact' from 'approximate' degeneracies is that of self-consistent solution of the generalized KS equations (equations (2) and (6)) for the external potential $v + \eta \, \delta v$ with $\eta \to 0$. This self-consistent calculation already indicates that in general χ_0, and in consequence χ, does not describe some entirely inherent property of the unperturbed interacting system, this being in stark contrast with the commonly held view (see above). We have to emphasize that the degeneracy of the KS orbitals at μ has no (at least not to our knowledge) direct bearing on the possible degeneracy of the lowest-lying many-body eigenstate of the *interacting* system. Conversely, for the (average) ND pertaining to some ensemble of degenerate GSs of an interacting system, the degeneracy of the corresponding KS orbitals at μ becomes unavoidable (excluding some specific cases in which some linear dependencies lead to some cancellations (Levy and Perdew 1985)), since such densities cannot correspond to pure states, either interacting or non-interacting.

Following the explicit self-consistent calculation for $v + \eta \, \delta v$, $\eta \to 0$, for a given $\delta v(r)$ (see above), we know which of the possible degeneracies at μ are exact. We signify the quantities pertaining to the self-consistent problem associated with $v + \eta \, \delta v$, $\eta \to 0$, by a tilde: $\widetilde{\psi}_i(r), \widetilde{\varepsilon}_i, \widetilde{\mu}$ and $\widetilde{f}_i$. These quantities are *all* functionals of δv and, except *some* of the $\widetilde{f}_i$s, approach the same limits as $\eta \to 0$ (the limits for the wavefunctions are defined up to unitary transformations), irrespective of the local function $\delta v'$ substituted for δv in $v + \eta \, \delta v$; as we have mentioned above, the changes in the f_is associated with $\varepsilon_i = \mu$ crucially depend

on the symmetry group of δv (this in so far as the irreducible representation, to which the degenerate orbitals at μ belong, is concerned). For the *linear* variation in n in equation (6) we have

$$\delta_1 n(\boldsymbol{r}) = \sum_i^< \left\{ [\delta_1 \widetilde{\psi}_i(\boldsymbol{r})] \widetilde{\psi}_i^*(\boldsymbol{r}) + \widetilde{\psi}_i(\boldsymbol{r})[\delta_1 \widetilde{\psi}_i^*(\boldsymbol{r})] \right\}$$

$$+ \sum_i^= \widetilde{f}_i \left\{ [\delta_1 \widetilde{\psi}_i(\boldsymbol{r})] \widetilde{\psi}_i^*(\boldsymbol{r}) + \widetilde{\psi}_i(\boldsymbol{r})[\delta_1 \widetilde{\psi}_i^*(\boldsymbol{r})] \right\} + \sum_i^= [\delta_1 \widetilde{f}_i] |\widetilde{\psi}_i(\boldsymbol{r})|^2 \qquad (11)$$

where $\sum_i^<$ stands for $\sum_{i;\widetilde{\varepsilon}_i < \widetilde{\mu}}$ and $\sum_i^=$ for $\sum_{i;\widetilde{\varepsilon}_i = \widetilde{\mu}}$. Variations in *all* $\widetilde{f}_i$s, in contrast to those in possibly *some* of the f_is, are smooth (in view of our conventions (see the text following equation (6)), the set $\{\widetilde{f}_i | \widetilde{\varepsilon}_i = \widetilde{\mu}, \forall i\}$ may be empty). With $\delta_1 \widetilde{\psi}_i$ orthogonal to $\widetilde{\psi}_i$, completeness of $\{\widetilde{\psi}_i | \forall i\}$ allows us to write

$$\delta_1 \widetilde{\psi}_i(\boldsymbol{r}) = \sum_{j; j \neq i} \alpha_{j,i}[\delta v] \widetilde{\psi}_j(\boldsymbol{r})$$

with the coefficients to be determined by first-order perturbation theory or degenerate perturbation theory, with δv being the perturbation, depending on whether $\widetilde{\psi}_i$ is non-degenerate or belongs to some manifold of degenerate eigenstates, respectively. In view of δv, and apparently not δv_{eff} (see equation (9)), playing the role of the perturbation potential, we point out that since $\delta_1 \widetilde{\psi}_i$ stands for the *non-self-consistent* first-order change in $\widetilde{\psi}_i$, the associated $\delta_1 n$ does *not* enter in the argument $[n]$ of $v_{eff}[n]$ in equation (2), so that *within the present context* δv and δv_{eff} are interchangeable. From these $\delta_1 \widetilde{\psi}_i$s, perturbation results for $\delta_1 n_1(\boldsymbol{r})$ and $\delta_1 n_2(\boldsymbol{r})$, corresponding to the first term and the second term on the right-hand side of equation (11) respectively, are easily obtained and thus the associated $\chi_{0;k}(\boldsymbol{r}, \boldsymbol{r}') := \delta_1 n_k(\boldsymbol{r})/\delta v(\boldsymbol{r}'), k = 1, 2$, are readily determined (see equation (9)).

Through some straightforward algebra one obtains

$$\chi_{0;1}(\boldsymbol{r}, \boldsymbol{r}') = 2 \sum_i^> \sum_j^< \frac{\widetilde{\psi}_i(\boldsymbol{r}) \widetilde{\psi}_i^*(\boldsymbol{r}') \widetilde{\psi}_j(\boldsymbol{r}') \widetilde{\psi}_j^*(\boldsymbol{r})}{\widetilde{\varepsilon}_j - \widetilde{\varepsilon}_i} \qquad (12)$$

which is the standard expression employed for the *total* χ_0 and indeed $\chi_{0;1}$ coincides with this for pure-state non-interacting v-rep GS NDs; in such an event $M = 0$ and the tildes on $\widetilde{\psi}_i$s and $\widetilde{\varepsilon}_i$s can be discarded (see our conventions following equation (6) above). It can easily be verified that $\chi_{0;1}(\boldsymbol{r}, \boldsymbol{r}') = \chi_{0;1}(\boldsymbol{r}', \boldsymbol{r})$ (we assume that for each term on the right-hand side of equation (12) corresponding to some (i, j), the associated time-reversed term, corresponding to $(\bar{i}, \bar{j})$, is also included; that is, we do not allow spontaneous breaking of the time-reversal symmetry).

For determining $\chi_{0;2}$ we have to make use of the degenerate perturbation theory. As indicated above, the degeneracies involved here (i.e. those corresponding to $\widetilde{\varepsilon}_i = \widetilde{\mu}$) are exact, that is they are not removed at any order of the perturbation theory. We denote the number of the degenerate states at $\widetilde{\mu}$ by $g_{\widetilde{\mu}}$ ($\equiv \sum_i^= 1$) and employ capital letters for their subscripts; thus

$$\{\widetilde{\psi}_I | I = 1, \ldots, g_{\widetilde{\mu}}\} \equiv \{\widetilde{\psi}_{N - \widetilde{M} + i} | i = 1, \ldots, g_{\widetilde{\mu}}\}$$

where $\widetilde{M} = \sum_i^= \widetilde{f}_i$. From the rudiments of the degenerate perturbation theory (in respect of some specific features of our present consideration, perhaps most explicitly discussed by Byron and Fuller 1969), it follows that owing to the exactness of the degeneracies, δv does *not* induce any observable transitions inside the manifold of degenerate eigenstates at $\widetilde{\mu}$. As a result, in so far as calculations are concerned, the only consequence of the

degeneracy of these states is the necessity to obtaining the (unique) unitary (or orthogonal) transformation amongst these eigenfunctions which renders application of the (degenerate) perturbation theory meaningful; we denote the appropriately transformed eigenfunctions by superscript (0), $\widetilde{\psi}_i^{(0)}(r)$. We have

$$\widetilde{\psi}_I^{(0)} = \sum_{J=1}^{g_{\widetilde{\mu}}} \beta_J^{(I)} \widetilde{\psi}_J.$$

This transformation is effected through solution of the eigenvalue problem

$$\sum_{J=1}^{g_{\widetilde{\mu}}} (\widetilde{\psi}_I, \delta v\, \widetilde{\psi}_J) \beta_J^{(K)} = \widetilde{\varepsilon}_I^{(1)} \beta_I^{(K)} \qquad I, K = 1, \ldots, g_{\widetilde{\mu}}$$

where $(\phi, A\varphi) := \int d^3 r\; \phi^*(r) A(r) \varphi(r)$ and $\widetilde{\varepsilon}_I^{(1)}$ denotes the first-order *correction* to $\widetilde{\varepsilon}_I$. The exactness of the degeneracy at $\widetilde{\mu}$ implies that this correction is the same for *all* $I \in \{1, \ldots, g_{\widetilde{\mu}}\}$; we have $(\widetilde{\psi}_I, \delta v\, \widetilde{\psi}_J) = \widetilde{e} \delta_{I,J}$, with $\widetilde{\varepsilon}_{\widetilde{\mu}}^{(1)} \equiv \widetilde{e}$, independently of I (evidently $\widetilde{e} \to 0$ as $\|\delta v\| \to 0$; the state independence of $\widetilde{e}$ implies that δv has a constant projection onto the subspace $\{\widetilde{\psi}_I | I = 1, \ldots, g_{\widetilde{\mu}}\}$). Further, normalization of the eigenfunctions implies that $\beta_I^{(J)} = \delta_{I,J}$, so $\widetilde{\psi}_I^{(0)} \equiv \widetilde{\psi}_I$. Now from the degenerate perturbation theory, for $\chi_{0;2}$ we readily obtain

$$\chi_{0;2}(r, r') = 2 \left\{ \sum_I \widetilde{f}_I \widetilde{\psi}_I(r) \widetilde{\psi}_I^*(r') \right\} \sum_j^{\neq} \frac{\widetilde{\psi}_j(r') \widetilde{\psi}_j^*(r)}{\widetilde{\mu} - \widetilde{\varepsilon}_j} \tag{13}$$

where $\sum_j^{\neq}$ stands for $\sum_{j;\widetilde{\varepsilon}_j \neq \widetilde{\mu}}$. It can easily be verified that $\chi_{0;2}(r, r') = \chi_{0;2}(r', r)$ (see the comment following equation (12)).

For calculating the third, and the last, contribution to χ_0, i.e. $\chi_{0;3}(r, r') := \delta_1 n_3(r) / \delta v(r')$ with $\delta_1 n_3$ denoting the last term on the right-hand side of equation (11), we proceed as follows. The variations δv and $\delta_1 n$ are related through $\delta v(r) = \int d^3 r'\, \chi_0^{-1}(r, r') \delta_1 n(r')$ (recall that in the present context $\delta v \equiv \delta v_{eff}[n]$). Further, since δv is local, from the first-order perturbation theory we have

$$\delta_1 \widetilde{\varepsilon}_i = \int d^3 r\; |\widetilde{\psi}_i(r)|^2\, \delta v(r).$$

Making use of the last expression for $\delta v(r)$ and the fact that $\delta_1 \widetilde{\varepsilon}_I \equiv \widetilde{\varepsilon}_I^{(1)} = 0$, $I = 1, \ldots, g_{\widetilde{\mu}}$ (in view of the fact that $\int d^3 r'\, \chi_0(r, r') = 0$ (see the paragraph following equation (19) below), which holds equally when χ_0 is replaced by χ_0^{-1}, this δv has zero average, so that the above-introduced $\widetilde{e}$ is identically vanishing), we obtain the following 'linear' (see further on) equation for $\{\delta_1 \widetilde{f}_I | I = 1, \ldots, g_{\widetilde{\mu}}\}$:

$$\sum_{J=1}^{g_{\widetilde{\mu}}} (\mathcal{A})_{I,J} (\delta_1 \widetilde{f}_J) = \gamma_I \qquad I = 1, \ldots, g_{\widetilde{\mu}} \tag{14}$$

where

$$(\mathcal{A})_{I,J} := \int d^3 r\; d^3 r'\; |\widetilde{\psi}_I(r)|^2 \chi_0^{-1}(r, r') |\widetilde{\psi}_J(r')|^2 \tag{15}$$

$$\gamma_I := - \int d^3 r\; d^3 r'\; |\widetilde{\psi}_I(r)|^2 \chi_0^{-1}(r, r') \sum_j^{\leqslant} \widetilde{f}_j \delta_1 |\widetilde{\psi}_j(r')|^2. \tag{16}$$

Here $\sum_j^{\leqslant}$ stands for $\sum_{j;\widetilde{\varepsilon}_j \leqslant \widetilde{\mu}}$. The solution $\delta_1 \widetilde{f}_I$ of equation (14) can formally be written as

$$\delta_1 \widetilde{f}_I = \sum_J (\mathcal{A}^{-1})_{I,J} \gamma_J$$

(see the paragraph preceding the concluding remarks). From equation (11) it is seen that

$$\sum_j^{\leqslant} \widetilde{f}_j \left\{ \delta_1 |\widetilde{\psi}_j(\boldsymbol{r})|^2 / \delta v(\boldsymbol{r}') \right\} = \chi_{0;1}(\boldsymbol{r}, \boldsymbol{r}') + \chi_{0;2}(\boldsymbol{r}, \boldsymbol{r}')$$

hence

$$\chi_{0;3}(\boldsymbol{r}, \boldsymbol{r}') = -\int \mathrm{d}^3 r_1 \, \mathrm{d}^3 r_2 \, \mathcal{D}(\boldsymbol{r}, \boldsymbol{r}_1) \chi_0^{-1}(\boldsymbol{r}_1, \boldsymbol{r}_2) \left\{ \chi_{0;1}(\boldsymbol{r}_2, \boldsymbol{r}') + \chi_{0;2}(\boldsymbol{r}_2, \boldsymbol{r}') \right\} \tag{17}$$

where

$$\mathcal{D}(\boldsymbol{r}, \boldsymbol{r}_1) := \sum_{I,J} |\widetilde{\psi}_I(\boldsymbol{r})|^2 (\mathcal{A}^{-1})_{I,J} |\widetilde{\psi}_J(\boldsymbol{r}_1)|^2. \tag{18}$$

Equation (17) can be transformed into the following, more appealing, form:

$$\chi_{0;3} = \chi_0 - \chi_0 (\chi_0 - \mathcal{D})^{-1} \chi_0 \equiv -(I - \mathcal{D}\chi_0^{-1})^{-1} \mathcal{D}. \tag{19}$$

The dependence of both $\mathcal{D}$ and $\chi_0 \equiv \chi_{0;1} + \chi_{0;2} + \chi_{0;3}$ on $\chi_{0;3}$ implies that $\chi_{0;3}$ has to be obtained through a self-consistent calculation. One noteworthy conclusion that can be drawn from equation (19) is that because $\chi_0(\boldsymbol{r}, \boldsymbol{r}') = \chi_0(\boldsymbol{r}', \boldsymbol{r})$ and $\mathcal{D}(\boldsymbol{r}, \boldsymbol{r}') = \mathcal{D}(\boldsymbol{r}', \boldsymbol{r})$, the equality $\chi_{0;3}(\boldsymbol{r}, \boldsymbol{r}') = \chi_{0;3}(\boldsymbol{r}', \boldsymbol{r})$ holds.

Before concluding this work, we should like to point out that χ_0 is singular: it possesses a zero eigenvalue corresponding to a constant eigenvector; this can readily be verified from the fact that $\chi_{0;k}(\boldsymbol{r}, \boldsymbol{r}')$, $k = 1, 2, 3$ (in equations (12), (13) and (17)), satisfies $\int \mathrm{d}^3 r' \, \chi_{0;k}(\boldsymbol{r}, \boldsymbol{r}') = 0$. The standard technique for dealing with the (quasi-) inverse of χ_0, which we encounter in equations (15), (16) and (17), is that of singular-value decomposition, SVD (see, e.g., Stoer and Bulirsch 1980). It is important to note that $\chi_{0;1}$ is negative semi-definite (to see this, write the right-hand side of equation (12) as

$$2 \sum_i^{>} \sum_j^{<} \{\widetilde{\psi}_i(\boldsymbol{r}) \widetilde{\psi}_j^*(\boldsymbol{r})\} \{\widetilde{\psi}_i(\boldsymbol{r}') \widetilde{\psi}_j^*(\boldsymbol{r}')\}^* / (\widetilde{\varepsilon}_j - \widetilde{\varepsilon}_i)$$

and recognize that the denominator is always negative), whereas $\chi_{0;2}$ in addition to the above-indicated zero eigenvalue has both positive and negative eigenvalues (the energy denominator in equation (13) has no definite sign). This implies that χ_0 *can* have positive eigenvalues (see below).

In conclusion, we have determined the density–density correlation function χ_0 appropriate to the generalized 'non-interacting' KS system pertinent to the *local* external potential v. By construction, the ND pertaining to an ensemble of degenerate GSs of this system is identical with the GS ND of the interacting system of electrons moving in the force field of v. In cases in which the GS ND of the interacting system is pure-state non-interacting v-rep (or equivalently, the GS of the above-mentioned KS system is non-degenerate), χ_0 coincides with the zeroth-order term in the many-body perturbation expansion for the density–density correlation function χ of the fully interacting system, with the 'non-interacting' Hamiltonian being the conventional KS Hamiltonian. For *proper* ensemble v-rep NDs, on the other hand, this non-degenerate many-body perturbation theory fails and thus χ_0 cannot be viewed as a zeroth-order approximation to χ within the context of the many-body perturbation theory. Although calculation of χ in terms of χ_0 requires knowledge

of $C := v_c + K_{xc}$ (see equation (10)) and the exact $K_{xc}[n]$ (see equation (7)) is unknown (it is known for instance within the LDA: $K_{xc}^{LDA}(r, r') = \{d\mu_{xc}(n(r))/dn(r)\}\delta(r - r')$ where $\mu_{xc}(n(r))$ stands for $v_{xc}^{LDA}(r; [n])$), it is important to realize that complete neglect of $K_{xc}[n]$ results in the random-phase approximation (RPA) for χ and in many instances this approximation is already very satisfactory.

The commonly used RPA, as opposed to that in terms of χ_0 calculated in this work, does not take account of the fact that the GS ND of an interacting system may be proper ensemble v-rep. An important observation is then that for systems whose GS ND is not pure-state non-interacting v-rep, the commonly used χ^{RPA} does *not* approach the exact χ in the limit of weak electron–electron interaction (or high density), whereas the RPA for χ based upon χ_0 as considered in the present work *always* approaches the correct limit.

The present χ_0 is in general a functional of the externally applied perturbation potential. We have established that the symmetry of this potential is of significant influence on the exact form of χ_0. Work to be published (Farid 1997) shows that the *static* χ_0 considered here plays a significant role within a framework designed for calculating energies and NDs of N-electron *excited* states of interacting systems. To give some appreciation of this matter, suffice it to say that according to a theorem due to Perdew and Levy (1985), N-electron excited states whose NDs are pure-state non-interacting v-rep form a *proper* subset of all N-electron excited states.

Above we have pointed out that, in contrast to the commonly used χ_0 (which coincides with our $\chi_{0;1}$ in equation (12)), our present χ_0 may have positive eigenvalues. In view of this, let us consider the static dielectric response function (sometimes also referred to as the 'test-charge' dielectric function) $\mathcal{E} := I - v_c P$ where P stands for the static polarization function. It can be shown that $P = (I + \chi v_c)^{-1}\chi$ (or $\chi = (I - P v_c)^{-1}P$), so that within the framework of the RPA $\mathcal{E}^{RPA} = I - v_c P^{RPA}$ holds with $P^{RPA} \equiv \chi_0$. The negative semi-definiteness of the conventional χ_0 implies that all eigenvalues of the conventional $\mathcal{E}^{RPA}$ are larger than or equal to unity; this is contrary to the exact case in which $\mathcal{E}$ can in addition possess *negative* eigenvalues (Kirzhnits 1976, Dolgov *et al* 1981, Car *et al* 1981). Negative eigenvalues are excluded only in the long-wavelength limit (in other words, $(\phi, \mathcal{E}\phi) \not< 0$ for a function $\phi(r)$ whose Fourier spectral weight $\bar{\phi}(q)$ is vanishing for $|q| > q_0$ where q_0 is smaller than the inverse of some macroscopic length scale in the system) and occurrence of these does not imply thermodynamic instability (Kirzhnits 1976); rather, these eigenvalues are of relevance to the formation of the Cooper pairs and the appearance of the phenomenon of superconductivity (Kirzhnits 1976, Dolgov *et al* 1981). Our above considerations with regard to sign of the eigenvalues of $\chi_0 \equiv \chi_{0;1} + \chi_{0;2} + \chi_{0;3}$ suggest that $\mathcal{E}^{RPA}$ calculated in terms of our present χ_0 incorporates some essential correlation effects that are absent in the conventional $\mathcal{E}^{RPA}$. Since this $\mathcal{E}^{RPA}$ is a functional of δv, which we have throughout this work considered to be externally applied, existence of possible negative eigenvalues of $\mathcal{E}^{RPA}$ will be dependent upon the form of δv. In the light of the connection between the above-mentioned negative eigenvalues and formation of the Cooper pairs, δv may be thought of as being induced by a static configuration of some particular combination of phonon modes in an otherwise perfectly regular system. We should like to emphasize however, that since we have *not* studied in any depth the contribution of $\chi_{0;2} + \chi_{0;3}$ for systems in the thermodynamic limit, our discussions with regard to the possible negative eigenvalues of $\mathcal{E}^{RPA} = I - v_c(\chi_{0;1} + \chi_{0;2} + \chi_{0;3})$ and the correspondence of these with the phenomenon of superconductivity should be viewed as being merely suggestive at this stage (it is however evident that when the Fermi surface in a metal does not allow for nesting, the contributions of $\chi_{0;2}$ and $\chi_{0;3}$ will be vanishingly small).

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