Density Functional Theory for Quasiparticle Properties

D. Van Neck

Laboratory of Theoretical Physics, Ghent University, Belgium

Abstract. A framework is proposed to construct the ground-state energy and density matrix of an N-electron system by solving selfconsistently a set of single-particle equations. The method is based on separating the Green's function into a quasi-particle part and a background part, and expressing only the background part as a functional of the local density or the density matrix. The calculated single-particle energies and wave functions have a clear physical interpretation as quasiparticle energies and orbitals. Apart from Hartree-Fock, also the standard Kohn-Sham DFT scheme is embedded as a special case. Several advantages of such an approach are pointed out, and possible implementations are explored.

1 Introduction

The power of the Kohn-Sham (KS) implementation [1] of density functional theory (DFT [2]) lies in its ability to incorporate complex many-body correlations (beyond Hartree-Fock) in a computational framework that is not any more difficult than the Hartree-Fock (HF) equations. In practice this means one has to solve single-particle Schrödinger equations, with local or non-local potentials, in an iterative self-consistency loop. This simplicity makes KS-DFT the only feasible approach in many modern applications of electronic structure theory.

The present implementations of DFT can handle short-range interelectronic correlations quite well, but often fail when dealing with near-degenerate systems characterized by a small particle-hole gap. This seems to indicate that KS-DFT does not accurately describe the Fermi surface if it deviates significantly from the noninteracting one. In this respect, one of the most glaring inadequacies of KS-DFT is the fact that the physically important concept of quasiparticles is missing. Even formal knowledge of the exact exchange-correlation energy functional would only lead to the total energy and the density, since the individual KS orbitals have no special significance. An exception is the HOMO orbital and energy which govern the asymptotic tail of the density.

Quasiparticle (QP) excitations in the Landau-Migdal sense [3, 4] form a well-known concept in many-body physics. They are most readily understood as the relics of the single-particle (s.p.) excitations in the noninteracting system when the interaction is turned on [5–7]. In most electronic systems, or more generally in all normal Fermi systems, the bulk of the s.p. strength (i.e. the transition strength related to the removal or addition of a particle) is concentrated in QP states. Especially

near the Fermi surface, the QP states represent the dominant physical feature and should be described properly in any appropriate single-particle theory.

The QP orbitals form a complete, linear independent, but generally nonorthogonal set. The completeness and linear independence follows from the fact that the QP states evolve from the set of single-particle eigenstates of a noninteracting Hamiltonian. Near the Fermi surface they coincide with the electron attachment states or with the dominant ionization states. Further away from the Fermi surface, QP states may acquire a width and correspond not to a single state but to a group of states in the $(N \pm 1)$-electron system characterized by rather pure one-hole or one-particle structure. The QP states have reduced s.p. strength (i.e. the normalization of the QP orbitals is less than unity). Note that QP orbitals and strengths (at least near the Fermi surface) are experimentally accessible using, e.g., electron momentum spectroscopy [8].

It is our aim to develop formally exact single-particle equations whose solutions can be interpreted as the QP energies and orbitals, and to explore how approximations can be introduced by the modelling of small quantities in terms of functionals. The resulting formalism will be called QP-DFT [9] and yields, apart from the QP orbitals and energies, also the total energy and the density matrix of the system.

2 The Quasiparticle Concept

We initially keep the discussion as general as possible, and consider a normal (non-superconducting) Fermi system with Hamiltonian $\hat{H} = \hat{H}_0 + \hat{V}$, where $\hat{H}_0$ contains the kinetic energy and external potential and $\hat{V}$ is the two-particle interaction. The s.p. propagator in the energy representation is defined as

$$G(\alpha, \beta; E) \equiv \sum_n \frac{(z_n^{(+)})_\alpha (z_n^{(+)})_\beta^*}{E - \epsilon_n^{(+)} + i\eta} + \sum_n \frac{(z_n^{(-)})_\alpha (z_n^{(-)})_\beta^*}{E - \epsilon_n^{(-)} - i\eta}. \tag{1}$$

where $\eta > 0$ is an infinitesimal convergence parameter. The poles of the propagator are given by $\epsilon_n^{(\pm)} = \pm(E_n^{N\pm 1} - E_0^N)$ and the the s.p. transition amplitudes read

$$(z_n^{(+)})_\alpha = \langle \Psi_0^N | a_\alpha | \Psi_n^{N+1} \rangle; \quad (z_n^{(-)})_\alpha = \langle \Psi_n^{N-1} | a_\alpha | \Psi_0^N \rangle. \tag{2}$$

Here $\alpha, \beta, ..$ label the elements of a complete orthonormal basis set of s.p. states, the second-quantization operators a_α $(a_\beta^\dagger)$ remove (add) a particle in state α (β). An exact eigenstates of the N-particle system are denoted by $|\Psi_n^N\rangle$ and its energy by E_n^N. Note that the amplitudes $z_n^{(\pm)}$ are usually called Dyson orbitals in the electronic context.

The poles $\epsilon_n^{(+)}$ and $\epsilon_n^{(-)}$ of the propagator are located in the addition domain $(\epsilon_0^{(+)}, +\infty)$ and the removal domain $(-\infty, \epsilon_0^{(-)})$, respectively. In a finite system both domains are separated by an energy interval $(\epsilon_0^{(-)}, \epsilon_0^{(+)})$. The width of the interval is the particle-hole gap,

$$\epsilon_0^{(+)} - \epsilon_0^{(-)} = E_0^{N+1} - 2E_0^N + E_0^{N-1} > 0, \tag{3}$$

where positivity is guaranteed by the assumed convexity of the E_0^N versus N curve. Only the interval is physically relevant, but for definiteness one can take the Fermi energy as the center of the interval,

$$\epsilon_F = \frac{1}{2}(\epsilon_0^{(-)} + \epsilon_0^{(+)}) = \frac{1}{2}(E_0^{N+1} - E_0^{N-1}). \tag{4}$$

In an infinite system one has $\epsilon_0^{(-)} = \epsilon_0^{(+)} = \epsilon_F$.

The (1-body) density matrix $[N^{(-)}]$ and removal energy matrix $[M^{(-)}]$ can be expressed in terms of the $\epsilon_n^{(-)}$ and $z_n^{(-)}$ as

$$N_{\alpha,\beta}^{(-)} \equiv \langle \Psi_0^N | a_\beta^\dagger a_\alpha | \Psi_0^N \rangle = \sum_n (z_n^{(-)})_\alpha (z_n^{(-)})_\beta^*$$

$$M_{\alpha,\beta}^{(-)} \equiv \langle \Psi_0^N | a_\beta^\dagger [a_\alpha, \hat{H}] | \Psi_0^N \rangle = \sum_n \epsilon_n^{(-)} (z_n^{(-)})_\alpha (z_n^{(-)})_\beta^* \tag{5}$$

Any one-body observable of interest can be calculated with the density matrix. The removal energy matrix allows in addition to calculate the total energy through the Migdal-Galitskii sum rule

$$E_0^N = \frac{1}{2}\text{Trace}([H_0][N^{(-)}] + [M^{(-)}]), \tag{6}$$

which can be obtained by exploiting the fact that $\text{Trace}[M^{(-)}] = \langle \Psi_0^N | \hat{H}_0 + 2\hat{V} | \Psi_0^N \rangle$. The removal part of the propagator is sufficient for these purposes. However, only the (inverse of) the full propagator has a meaningful perturbative expansion, which takes the form of the Dyson equation,

$$[G(E)]^{-1} = [G_0(E)]^{-1} - [\Sigma(E)], \tag{7}$$

where $[G_0(E)]$ is the noninteracting propagator corresponding to the Hamiltonian $\hat{H}_0$ and $[\Sigma(E)]$ is the (one fermion line) irreducible selfenergy. In an ab-initio calculation, the physics input is controlled by taking a suitable approximation for the selfenergy, but here the reasoning is in terms of the exact selfenergy. The latter plays the role of an energy-dependent s.p. potential.

The (1-body) density matrix $[N^{(-)}]$ (removal energy matrix $[M^{(-)}]$) is the zero'th (first) energy-weighted moment of the spectral distribution in the removal domain. Similar quantities can be defined in the addition domain,

$$N_{\alpha,\beta}^{(+)} \equiv \langle \Psi_0^N | a_\alpha a_\beta^\dagger | \Psi_0^N \rangle = \sum_n (z_n^{(+)})_\alpha (z_n^{(+)})_\beta^*$$

$$M_{\alpha,\beta}^{(+)} \equiv \langle \Psi_0^N | [a_\alpha, \hat{H}] a_\beta^\dagger | \Psi_0^N \rangle = \sum_n \epsilon_n^{(+)} (z_n^{(+)})_\alpha (z_n^{(+)})_\beta^*. \tag{8}$$

Taking the sum of addition and removal parts generates an extra anticommutator,

$$N_{\alpha,\beta} = N_{\alpha,\beta}^{(-)} + N_{\alpha,\beta}^{(+)} = \langle \Psi_0^N | \{a_\beta^\dagger a_\alpha\} | \Psi_0^N \rangle \tag{9}$$

$$M_{\alpha,\beta} = M_{\alpha,\beta}^{(-)} + M_{\alpha,\beta}^{(+)} = \langle \Psi_0^N | a_\beta^\dagger [a_\alpha, \hat{H}] | \Psi_0^N \rangle. \tag{10}$$

Writing the Hamiltonian as

$$\hat{H} = \sum_{\gamma\delta}\langle\gamma|H_0|\delta\rangle a_\gamma^\dagger a_\delta + \frac{1}{4}\sum_{\mu\nu\gamma\delta}\langle\mu\gamma|V|\nu\delta\rangle_{as}\, a_\mu^\dagger a_\gamma^\dagger a_\delta a_\nu, \qquad (11)$$

with $\langle\alpha\beta|V|\gamma\delta\rangle_{as} \equiv \langle\alpha\beta|V|\gamma\delta\rangle - \langle\alpha\beta|V|\delta\gamma\rangle$ the antisymmetrized interaction matrix element, the (anti)commutator on the right of Eq. (10) can be worked out explicitly as

$$\{a_\beta^\dagger,[a_\alpha,\hat{H}]\} = \langle\alpha|H_0|\beta\rangle + \sum_{\gamma\delta}\langle\alpha\gamma|V|\beta\delta\rangle_{as}a_\gamma^\dagger a_\delta. \qquad (12)$$

As a result, it is possible to express the sumrules in Eq. (10) in closed form as

$$N_{\alpha,\beta} = \delta_{\alpha,\beta}, \text{ or } [N] = [I], \qquad (13)$$
$$M_{\alpha,\beta} = \langle\alpha|H_0|\beta\rangle + \sum_{\gamma\delta}\langle\alpha\gamma|V|\beta\delta\rangle_{as}N_{\delta\gamma}^{(-)}, \text{ or } [M] = [H_0] + [\tilde{V}_{HF}],$$

where $[I]$ is the identity matrix. These expressions will be used extensively in the following. The term, $[\tilde{V}_{HF}]$, in Eq. (13) is the sum of all static (energy independent) selfenergy contributions, and has the form of the HF mean field, but evaluated with the exact density matrix $[N^{(-)}]$. A diagrammatical representation is provided by the first term in Figure 1.
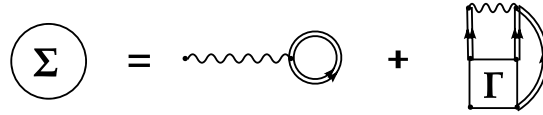

Figure 1. General structure of the exact self-energy $\Sigma(E)$ in terms of the exact 4-point vertex function Γ. The wavy line represents the antisymmetrized interaction, the double directed line is the exact propagator. The first term is the sum of all static selfenergy contributions $\tilde{V}_{HF}$, the second term involving Γ groups all energy-dependent contributions.

In normal Fermi systems, the bulk of the spectral strength is concentrated in quasiparticle (QP) states which, in the Landau-Migdal picture, evolve adiabatically from the $N \pm 1$ eigenstates of $\hat{H}_0$, and can be regarded as the elementary s.p. excitations in the interacting system. In its simplest form the QP contribution to the propagator can be written as a modified noninteracting propagator,

$$G_Q(\alpha,\beta;E) = \sum_{j=1}^{N}\frac{(z_{Qj})_\alpha(z_{Qj})_\beta^*}{E - \epsilon_{Qj} - iw_{Qj}} + \sum_{j=N+1}^{\infty}\frac{(z_{Qj})_\alpha(z_{Qj})_\beta^*}{E - \epsilon_{Qj} + iw_{Qj}} \qquad (14)$$

where $w_{Qj} > 0$ characterizes the width of the QP excitation at energy ϵ_{Qj}, and z_{Qj} is the corresponding QP orbital. The first term in Eq. (14) corresponds to excitations in the $(N-1)$-particle system, as indicated by the location of the poles in the upper

half-plane ($\text{Im}E > 0$). It contains the N lowest QP energies ϵ_{Qj} ($j = 1, .., N$), for which $\epsilon_{Qj} < \epsilon_F$. The higher QP states ($j = N + 1, .., \infty$) in the second term of Eq. (14) correspond to the ($N + 1$) system, as indicated by the location of the poles in the lower half-plane ($\text{Im}E < 0$), and have $\epsilon_{Qj} > \epsilon_F$.

The QP contribution to the sumrules in Eq. (13) is given by

$$[N_Q] = \sum_{j=1}^{\infty} z_{Qj} z_{Qj}^{\dagger}; \quad [M_Q] = \sum_{j=1}^{\infty} \epsilon_{Qj} z_{Qj} z_{Qj}^{\dagger}. \tag{15}$$

Note that the QP width does not contribute to the 0th and 1st moment, and drops out from all subsequent considerations.

The QP contribution to the separate $[N^{(\pm)}]$ and $[M^{(\pm)}]$ reads

$$[N_Q^{(-)}] = \sum_{j=1}^{N} z_{Qj} z_{Qj}^{\dagger}; \quad [M_Q^{(-)}] = \sum_{j=1}^{N} \epsilon_{Qj} z_{Qj} z_{Qj}^{\dagger}, \tag{16}$$

and similarly for

$$[N_Q^{(+)}] = \sum_{j=N+1}^{\infty} z_{Qj} z_{Qj}^{\dagger}; \quad [M_Q^{(+)}] = \sum_{j=N+1}^{\infty} \epsilon_{Qj} z_{Qj} z_{Qj}^{\dagger}. \tag{17}$$

3 Quasiparticle Equations

For the following it is important to realize that, given arbitrary hermitian matrices $[N_Q]$ and $[M_Q]$ with $[N_Q]$ positive-definite, one can always write the unique decomposition of Eq. (15). This can be achieved by constructing the unique basis that solves the (generalized) eigenvalue problem

$$[M_Q]u_j = \lambda_j [N_Q]u_j; \quad u_j^{\dagger}[N_Q]u_k = \delta_{j,k}, \tag{18}$$

where $[N_Q]$ plays the role of a metric matrix; the QP energies and orbitals given by $\epsilon_{Qj} = \lambda_j$ and $z_{Qj} = [N_Q]u_j$ then fulfill Eq. (15).

The eigenvalue problem in Eq. (18) can be considered as a set of s.p. equations determining the QP orbitals and energies. We now rewrite the unknown operators $[N_Q]$ and $[M_Q]$ in a more useful form that suggests possible approximation schemes.

Since the QP contribution is dominant, it makes sense to isolate it, and concentrate on the residual small 'background' contribution,

$$[N] = [N_Q] + [N_B]; \quad [M] = [M_Q] + [M_B], \tag{19}$$

where the total energy integrals $[N_B] = [N_B^{(-)}] + [N_B^{(+)}]$ and $[M_B] = [M_B^{(-)}] + [M_B^{(+)}]$ can again be split in a removal and addition part. Note that the matrices $[N]$ and $[M]$ on the left side of Eq. (19) are known in closed form, so it follows that

$$[N_Q] = [I] - [N_B], \tag{20}$$

$$[M_Q] = [H_0] + [\tilde{V}_{HF}] - [M_B]. \tag{21}$$

One then arrives at the remarkable conclusion that modelling the background contributions $[M_B^{(\pm)}]$ and $[N_B^{(\pm)}]$ as a functional of e.g. the density matrix $[N^{(-)}]$, is sufficient to generate a selfconsistent set of s.p. equations. Using Eqs. (20-21) the eigenvalue problem in Eq. (18) can be expressed as

$$([H_0] + [\tilde{V}_{HF}\{N^{(-)}\}] - [M_B\{N^{(-)}\}])u_j = \lambda_j([I] - [N_B\{N^{(-)}\}])u_j, \tag{22}$$

where the functional dependency of $[M_B]$ and $[N_B]$ is indicated between braces. Note that also the HF-like potential $[\tilde{V}_{HF}]$ is by definition [see Eq. (13)] expressed in terms of the density matrix, as indicated in Eq. (22).

Having an initial estimate for $[N^{(-)}]$ allows to construct the matrices $[N_B]$ and $[M_B]$, as well as the HF-like potential $[\tilde{V}_{HF}]$. The eigenvalue problem in Eq. (22) can now be solved, yielding QP energies $\epsilon_{Qj} = \lambda_j$ and orbitals $z_{Qj} = ([I] - [N_B\{N^{(-)}\}])u_j$. The N solutions with lowest energy represent excitations in the $N-1$ system, and should be used to update the density matrix,

$$[N_{\text{new}}^{(-)}] = \sum_{j=1}^{N} z_{Qj} z_{Qj}^{\dagger} + [N_B^{(-)}\{N^{(-)}\}]. \tag{23}$$

This closes the selfconsistency loop, which can be iterated to convergence. The total energy then follows from Eq. (6),

$$E_0^N = \frac{1}{2} \sum_{j=1}^{N} z_{Qj}^{\dagger}([H_0] + \epsilon_{Qj})z_{Qj} + \frac{1}{2}\text{Trace}\left([H_0][N_B^{(-)}\{N^{(-)}\}] + [M_B^{(-)}\{N^{(-)}\}]\right). \tag{24}$$

The above formalism, henceforth called quasiparticle DFT (QP-DFT), generates the total energy, the density matrix, and the individual QP energies and orbitals, starting from a model for the background contributions $[M_B^{(\pm)}]$ and $[N_B^{(\pm)}]$ as a functional of the density matrix. It is intuitively clear that this is a reasonable strategy: the external potential appears directly in the QP hamiltonian $[M] - [M_B]$ through the $[H_0]$ term of Eq. (13), and primarily influences the position of the QP peaks. One may then assume the background part to be generated by 'universal' electron-electron correlations, and to be a good candidate for modelling.

We now show that both HF and KS-DFT theory are included in the general QP-DFT treatment.

For HF this is rather obviously achieved by setting all background quantities $[M_B^{(\pm)}]$ and $[N_B^{(\pm)}]$ equal to zero in Eq. (22). Since the metric matrix on the right of Eq. (22) is now simply the identity matrix, one has $z_{Qj} = u_j$ and the QP orbitals form an orthonormal set obeying $([H_0] + [\tilde{V}_{HF}])z_{Qj} = \epsilon_{Qj} z_{Qj}$. The matrix $[\tilde{V}_{HF}]$ is given by Eq. (13) where the density matrix $[N^{(-)}]$ in the present approximation follows from Eq. (23) with $[N_B^{(-)}] = 0$, i.e. $[N^{(-)}] = \sum_{j=1}^{N} z_{Qj} z_{Qj}^{\dagger}$. One can see

that $[M] = [H_0] + [\tilde{V}_{HF}]$ is just the ordinary HF hamiltonian, and the total energy obtained from Eq. (24) by setting $[N_B^{(-)}] = [M_B^{(-)}] = 0$,

$$E_0^N = \frac{1}{2}\sum_{j=1}^{N}(z_{Qj}^\dagger[H_0]z_{Qj} + \epsilon_{Qj}) \tag{25}$$

is equivalent to the HF total energy.

The KS-DFT case is somewhat more difficult, but one also starts by setting $[N_B^{(\pm)}] = 0$ in Eq. (22), so the QP states z_{Qj} form an orthonormal set obeying

$$([H_0] + [\tilde{V}_H] + [\tilde{V}_F] - [M_B])z_{Qj} = \epsilon_{Qj}z_{Qj}. \tag{26}$$

Here the HF-like potential has been split into its direct and exchange components, $[\tilde{V}_{HF}] = [\tilde{V}_H] + [\tilde{V}_F]$. Again, both components only receive contributions from the occupied ($j = 1, .., N$) orbitals z_{Qj}. For the Coulomb interaction and taking as s.p. labels for the electrons the space coordinate and (third component of) spin, $\alpha \equiv \mathbf{r}m_s$, this reduces to the familiar expression

$$\tilde{V}_H(\mathbf{r}m_s, \mathbf{r}'m_s') = \delta_{m_s,m_s'}\delta(\mathbf{r}-\mathbf{r}')\sum_{j=1}^{N}\sum_{m_s''}\int d\mathbf{r}''\frac{|z_{Qj}(\mathbf{r}''m_s'')|^2}{|\mathbf{r}-\mathbf{r}''|}$$

$$\tilde{V}_F(\mathbf{r}m_s, \mathbf{r}'m_s') = -\sum_{j=1}^{N}\frac{z_{Qj}(\mathbf{r}m_s)z_{Qj}^*(\mathbf{r}'m_s')}{|\mathbf{r}-\mathbf{r}'|}. \tag{27}$$

Note that for compactness we continue to employ the general matrix notation used so far, with the understanding that sums over s.p. labels should be replaced by coordinate space integrations where appropriate. The total energy follows from Eq. (24) with $[N_B^{(\pm)}] = 0$,

$$E_0^N = \frac{1}{2}\sum_{j=1}^{N}(z_{Qj}^\dagger[H_0]z_{Qj} + \epsilon_{Qj}) + \frac{1}{2}\text{Trace}[M_B^{(-)}]. \tag{28}$$

The unknown $[M_B^{(\pm)}]$ should now be determined by identification with the results of a KS-DFT calculation.

We allow explicit dependence on the KS orbitals φ_{KSj}, and write the exchange-correlation energy functional as

$$E_{xc} = \sum_{j=1}^{N}\varphi_{KSj}^\dagger[\epsilon_{xc}]\varphi_{KSj}. \tag{29}$$

Specializing e.g. to a hybrid functional (the derivation for a functional with general orbital dependencies proceeds in a similar fashion) with a fraction β of exact exchange, the matrix $[\epsilon_{xc}]$ in coordinate-spin space reads,

$$\epsilon_{xc}(\mathbf{r}\, m_s, \mathbf{r}'\, m_s') = -\frac{\beta}{2} \sum_{j=1}^{N} \frac{\varphi_{KSj}(\mathbf{r}\, m_s)\varphi_{KSj}^*(\mathbf{r}'\, m_s')}{|\mathbf{r} - \mathbf{r}'|} \tag{30}$$
$$+\delta_{m_s, m_s'}\delta(\mathbf{r} - \mathbf{r}')f_\beta(\rho(\mathbf{r}), \nabla\rho(\mathbf{r})),$$

where the second term contains a local functional of the electron density $\rho(\mathbf{r})$ and its gradient (assuming for simplicity a spin-saturated system). The corresponding exchange-correlation potential $[V_{xc}]$, appearing in the KS equation, then reads

$$V_{xc}(\mathbf{r}\, m_s, \mathbf{r}'\, m_s') = -\beta \sum_{j=1}^{N} \frac{\varphi_{KSj}(\mathbf{r}\, m_s)\varphi_{KSj}^*(\mathbf{r}'\, m_s')}{|\mathbf{r} - \mathbf{r}'|} \tag{31}$$
$$+\delta_{m_s, m_s'}\delta(\mathbf{r} - \mathbf{r}')\{f_\beta + \rho\frac{\partial f_\beta}{\partial \rho} - \nabla \cdot (\rho\frac{\partial f_\beta}{\partial \nabla\rho})\}.$$

Identification of the orbitals and energies in the KS equation

$$([H_0] + [V_H] + [V_{xc}])\varphi_{KSj} = \epsilon_{KSj}\varphi_{KSj} \tag{32}$$

with those in Eq. (26) then requires

$$[M_B] = [V_F] - [V_{xc}]. \tag{33}$$

Identification of the KS total energy

$$E_0^N = \sum_{j=1}^{N} \varphi_{KSj}^\dagger([H_0] + [V_H])\varphi_{KSj} + E_{xc} \tag{34}$$
$$= \frac{1}{2}\sum_{j=1}^{N}(\varphi_{KSj}^\dagger[H_0]\varphi_{KSj} + \epsilon_{KSj}) + E_{xc} - \frac{1}{2}\sum_{j=1}^{N}\varphi_{KSj}^\dagger[V_{xc}]\varphi_{KSj}$$

with Eq. (28) requires

$$\text{Trace}[M_B^{(-)}] = \sum_{j=1}^{N}\varphi_{KSj}^\dagger(2[\epsilon_{xc}] - [V_{xc}])\varphi_{KSj}. \tag{35}$$

Choosing the $[M_B^{(\pm)}]$ operators as

$$[M_B^{(-)}] = [P](2[\epsilon_{xc}] - [V_{xc}])[P]; \quad [M_B^{(+)}] = [V_F] - [V_{xc}] - [M_B^{(-)}], \tag{36}$$

where $[P] = \sum_{j=1}^{N} z_{Qj}z_{Qj}^\dagger$ projects onto the occupied QP orbitals, fulfills the requirements of both Eq. (33) and of Eq. (35); this choice therefore leads to the same results as the KS-DFT approximation, for the total energy as well as the orbitals and orbital energies.

One concludes that the QP-DFT formulation is flexible enough to reproduce HF or KS-DFT results by specific choices of $[N_B^{(\pm)}]$ and $[M_B^{(\pm)}]$.

It should be clear that GF quantities like the propagator, spectral function, or selfenergy, are well-defined and can in principle be calculated exactly. Also the separation of the spectral strength into QP and background parts can be performed for any system. In fact, defining the QP part can usually be done in several ways which are all, however, equivalent at the Fermi surface. Note that the density matrix and the total energy only contain the 0th and 1st energy-weighted moment $[N^{(-)}]$ and $[M^{(-)}]$, and do not depend on the QP-background separation. As long as one sticks to one unique prescription, the QP orbitals and energies are well-defined quantities, and so are the background contributions $[N_B^{(\pm)}]$ and $[M_B^{(\pm)}]$. The fundamental expressions in Eq. (22-24) are therefore always valid. It should be stressed that the possibility of defining QP excitations in various ways is not a shortcoming of the present approach, but rather a reflection of the physical reality that QP excitations are only unambiguously defined near the Fermi surface, where the density of states in the $N \pm 1$ system is small. The complete description of the s.p. properties in an interacting many-body system is contained in the energy dependence of the spectral function. *Any* effective s.p. Hamiltonian can at most describe the peaks in the spectral function, i.e. identify the energy regions where the s.p. strength is concentrated and assign an average transition amplitude to this region.

4 Summary and Discussion

The concept of quasiparticles is an important tool to understand and describe normal Fermi systems. In this paper we developed a set of single-particle equations whose solutions correspond to the QP orbitals and energies. When the residual small background contributions are expressed as universal functionals of the density or density matrix, a single-particle selfconsistency problem (the QP-DFT scheme) is generated that can be easily solved for an approximate choice of the functionals.

The QP-DFT scheme would seem to offer many advantages as compared to KS-DFT. There is no need for the difference between the kinetic energy of the interacting systems and a reference system. All s.p. orbitals and energies have physical meaning, in contrast to the KS orbitals. The asymptotic behavior of the QP orbitals comes out correct, provided the background operators are short-ranged. On the down side: since we no longer have a sharp Fermi surface, particle-number conservation is not automatically guaranteed, and should be built into the functionals.

The fact that KS-DFT is built in as a special case is a very important feature of QP-DFT. In a sense, one cannot do worse than KS-DFT, since one adds more parameters to the model. Moreover, the new parameters are truly new degrees of freedom (the introduction of the metric matrix, allowing a softening of the Fermi surface), which cannot be mimicked by taking a more sophisticated KS functional.

The modelling of the background operators $[N_B^{(\pm)}]$, $[M_B^{(\pm)}]$ is basically virgin territory. One option would be to exploit the relation (36) with the KS formalism, using an existing XC functional form for $[M_B^{(\pm)}]$, adding a similar form for $[N_B^{(\pm)}]$, and (re)parametrize by fitting to total energies and ionization energies in a training set of atoms and molecules.

Alternatively, one could devise parametrizations by performing GF calculations on a series of test systems, and construct the background operators directly from the calculated spectral function. A step in this direction was taken in [10], where we applied an ab-initio selfenergy of the G_0W_0 type to a series of closed-shell atoms. The QP-DFT scheme outlined in the present paper was used in first iteration (no selfconsistency) to generate the first-order corrections to the HF picture. We then constructed a simple QP-DFT functional that depends only on HF quantities, but was able to reproduce the most important results of the underlying ab-initio model.

References

1. W. Kohn and L.J. Sham, *Phys. Rev. A* **140**, 1133 (1965).
2. P. Hohenberg and W. Kohn, *Phys. Rev. B* **136**, 864 (1964).
3. L.D. Landau, *JETP* **3**, 920 (1957); *JETP* **5**, 101 (1957); *JETP* **8**, 70 (1959).
4. A.B. Migdal, *Theory of Finite Fermi Systems and Applications to Atomic Nuclei* (John Wiley and Sons, New York, 1967).
5. A.L. Fetter and J.D. Walecka, *Quantum Theory of Many Particle Systems* (McGraw-Hill, New York, 1971).
6. W.H. Dickhoff and D. Van Neck, *Many-Body Theory Exposed: propagator description of many particle quantum mechanics* (World Scientific, Singapore, 2005).
7. C. Mahaux and R. Sartor, *Adv. Nucl. Phys.* **20**, 1 (1991).
8. E. Weigold and I.E. McCarthy, *Electron Momentum Spectroscopy* (Kluwer Academic/Plenum Publishers, New York, 1999).
9. D. Van Neck *et al.*, *Phys. Rev. A* **74**, 042501 (2006).
10. S. Verdonck, D. Van Neck, P.W. Ayers and M. Waroquier, *Phys. Rev. A* (2006) to be published.