Quasiparticle properties in a density functional framework

D. Van Neck

Laboratory of Theoretical Physics
Ghent University, Belgium

Overview

* Context

* DFT + Kohn-Sham

* Green's function theory

* Quasiparticles

* Theoretical derivation of QP-DFT
[Phys.Rev.A74, 042501 (2006)]

* Applications to nuclear and electronic structure.

Context

Non-relativistic many-body problem

Hamiltonian:

$$\hat{H} = \sum_{i=1}^{N} \left[-\frac{\hbar^2}{2m_i} \vec{\nabla}_i^{\,2} + V_{ext}(\vec{r_i}) \right] + \sum_{i<j=1}^{N} W(\vec{r_i}, \vec{r_j})$$

N-body wave function $\Psi(x_1, \ldots, x_N)$

Large dimension $\Rightarrow$ many-body methods:

Density functional theory, Green function perturbation theory, stochastic methods (Monte Carlo)...

DFT only feasible approach to handle electronic structure for complex systems

DFT+KS

* Based on existence of universal density functional $E_{xc}[\rho]$ (= "exchange-correlation energy functional").

* Electronic energy $E = T + E_{ee} + E_{ext} = T_{KS} + E_H + E_{ext} + E_{xc}$

* xc energy functional $E_{xc}[\rho] = (T - T_{KS}) + E_{ee} - E_H$, with $T_{KS}[\rho]$ = kinetic energy of noninteracting system with density ρ

* Minimize energy $\Rightarrow$ KS equations:

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + V_{KS}(\vec{r})\right]\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r}) \quad i = 1..N$$

* Unique local potental $V_{KS}(\vec{r}) = V_{ext}(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r})$ such that $\rho(\vec{r}) = \rho_{KS}(\vec{r}) = \sum_{i=1}^{N} |\phi_i(\vec{r})|^2$, where $V_{xc}(\vec{r}) = \frac{\delta E_{xc}}{\delta \rho(\vec{r})}$

Comment

•DFT has double role:
(1) As a theoretical tool: Assuming exact xc functional is known, one can derive insights and new relationships between various quantities (e.g. theory of reactivity indices).
(2) As a computational tool, more judged by practical performance than by considerations of exactness.
• "DFT-like" approaches: any recipe to describe many-electron system by solving single-electron problems (usually in self-consistency loop).
• DFT-KS has its problems $\Rightarrow$ interest in new approaches.

Why would more general type of DFT be useful?

- KS-DFT can treat short-range interelectronic correlations quite well, but fails for near degenerate systems with small particle-hole gap (e.g. dissociation limit of molecules)
- No adequate description of Fermi surface
- Concept of quasiparticles is missing in KS-DFT

Interest in generalized DFT scheme for quasiparticles.
Is there link with Green's function description?

GFT

Propagator $G(x,x';E) = \sum_n \frac{\varphi^*_{(+)n}(x')\varphi_{(+)n}(x)}{E-\epsilon_{(+)n}+i\eta} + \sum_n \frac{\varphi^*_{(-)n}(x')\varphi_{(-)n}(x)}{E-\epsilon_{(-)n}-i\eta}$

$$\varphi_{(-)n}(x) = \langle \Psi_n^{N-1}|a(x)|\Psi_0^N\rangle \quad \text{(removal amplitude)}$$
$$\varphi_{(+)n}(x) = \langle \Psi_0^{N}|a(x)|\Psi_n^{N+1}\rangle \quad \text{(addition amplitude)}$$
$$\epsilon_{(-)n} = E_0^N - E_n^{N-1} \quad \text{(removal energy)}$$
$$\epsilon_{(+)n} = E_n^{N+1} - E_0^N \quad \text{(addition energy)}$$

All are experimentally accessible quantities.

Energy spectrum of $N \pm 1$ system.
Overlap functions $[(\gamma, e),\ (e,\gamma),\ (e,2e)]$

Derived quantities

Density matrix:

$$N_{(-)}(x,x') = \sum_n \varphi^*_{(-)n}(x')\varphi_{(-)n}(x) = \langle \Psi_0^N | a^\dagger(x') a(x) | \Psi_0^N \rangle$$

Removal energy matrix

$$\begin{aligned} M_{(-)}(x,x') &= \sum_n \epsilon_{(-)n} \varphi^*_{(-)n}(x')\varphi_{(-)n}(x) \\ &= \langle \Psi_0^N | a^\dagger(x') [a(x), \hat{H}] | \Psi_0^N \rangle \end{aligned}$$

Total energy through Migdal-Galitskii relation:

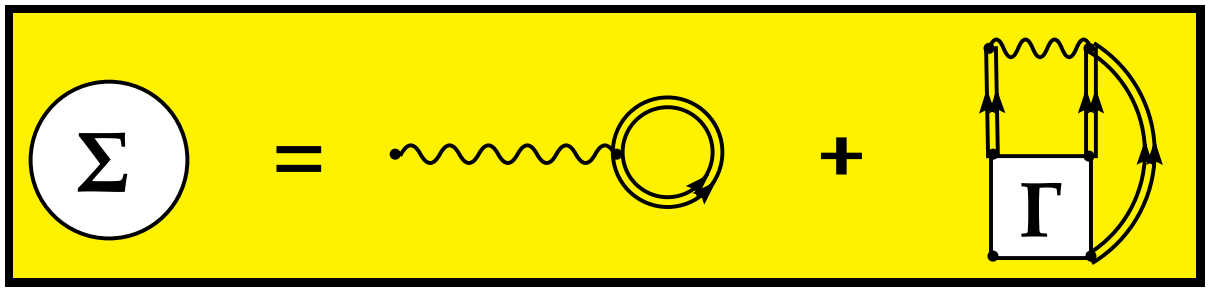
$$E_0^N = \frac{1}{2} \mathsf{Trace} \left\{ ([T] + [V_{ext}])[N_{(-)}] + [M_{(-)}] \right\}$$

Self-energy

* Dyson equation: $[G(E)] = [G_0(E)] + [G(E)][\Sigma(E)][G_0(E)]$

* $[G_0(E)]$ is non-interacting propagator ($[H_0] = [T] + [V_{ext}]$)

* $\Sigma(E)$ is irreducible self-energy: Energy-dependent, nonlocal, complex sp potential. Has well-defined perturbation expansion. Physics input can be controlled through approximation for Σ.



Spectral function

Contains equivalent information as propagator.

Distribution of single-particle strength over energy:

$$S(x,x';E) = \sum_n \delta(E-\epsilon_{(-)n})\varphi^*_{(-)n}(x')\varphi_{(-)n}(x) + \sum_n \delta(E-\epsilon_{(+)n})\varphi^*_{(+)n}(x')\varphi_{(+)n}(x)$$

Important 0th and 1st energy-weighted sumrules:

$$N(x,x') = \int dE S(x,x';E) = \langle \Psi_0^N | \{a^\dagger(x'), a(x)\} | \Psi_0^N \rangle$$

$$M(x,x') = \int dE E\, S(x,x';E) = \langle \Psi_0^N | \{a^\dagger(x'), [a(x), \hat{H}]\} | \Psi_0^N \rangle$$

Sumrules can be worked out as:

$$\begin{aligned} [N] &= [1] \\ [M] &= [T] + [V_{ext}] + [V_{HF}] \end{aligned}$$

where V_{HF} is Hartree-Fock type potential

$$V_{HF}(x,x') = \delta(x-x') \int dx'' \frac{N_{(-)}(x'',x'')}{|\vec{r}-\vec{r}''|} - \frac{N_{(-)}(x,x')}{|\vec{r}-\vec{r}'|}$$

but evaluated with the exact density matrix.

These sumrules are all that is needed for remainder. Complete energy dependence of spectral function is not needed.

Quasiparticles

- In normal Fermi systems: bulk of spectral strength resides in quasiparticle states (QP) states = elementary sp excitations, evolving adiabatically from the $N \pm 1$ eigenstates of unperturbed hamiltonian (Landau-Migdal picture).
$\Rightarrow$ in 1-1 correspondence with non-interacting sp states

- Characterized by position, strength, and width.

$$G_Q(x,x';E) = \sum_{j=1}^{N} \frac{z_{Qj}(x) z^*_{Qj}(x')}{E - \epsilon_{Qj} - iw_{Qj}} + \sum_{j=N+1}^{\infty} \frac{z_{Qj}(x) z^*_{Qj}(x')}{E - \epsilon_{Qj} + iw_{Qj}}$$

The concept of QP excitations is totally missing in KS-DFT, since the individual Kohn-Sham orbitals have no special significance.

Can we derive single-particle equations for the QP orbitals (QPDFT)?

QP contribution to 0th and 1st moment

• QP width does not contribute to 0th and 1st moment of spectral distribution: $[N_Q] = \sum_{j=1}^{\infty} z_{Qj} z_{Qj}^{\dagger}$; $[M_Q] = \sum_{j=1}^{\infty} \epsilon_{Qj} z_{Qj} z_{Qj}^{\dagger}$

Note 1: Given arbitrary, hermitian matrices $[N_Q]$ and $[M_Q]$ with $[N_Q]$ positive definite, one has unique decomposition.
How? Solve generalized eigenvalue problem

$$[M_Q]u_j = \lambda_j [N_Q] u_j; \qquad u_{Qj}^{\dagger} [N_Q] u_{Qk} = \delta_{j,k}$$

Then $\epsilon_{Qj} = \lambda_j$ and $z_{Qj} = [N_Q]u_j$ are solution.

Note 2: Split of QP in removal and addition part is obvious :

$$[N_{Q(-)}] = \sum_{j=1}^{N} z_{Qj} z_{Qj}^{\dagger}; \qquad [M_{Q(-)}] = \sum_{j=1}^{N} \epsilon_{Qj} z_{Qj} z_{Qj}^{\dagger}$$

Quasiparticle equations

* Split spectral function into dominant quasi-particle (QP) excitations and a residual small background part (which is a good candidate for "universal" modelling).

* Full energy dependence of $[S_B(E)]$ is not needed, only 0th and 1st order moment:

$$[N] = [N_Q] + [N_B]; \;\; [M] = [M_Q] + [M_B]$$

Since $[N]$ and $[M]$ are known, modeling of the (small) contributions $[N_B]$ and $[M_B]$ as a functional of the density matrix is sufficient to generate selfconsistency problem.

$$\begin{aligned} [M_Q]u_j &= \lambda_j [N_Q]u_j \\ ([H_0] + [V_{HF}\{N_{(-)}\}] - [M_B\{N_{(-)}\}])u_j &= \lambda_j([I] - [N_B\{N_{(-)}\}])u_j \end{aligned}$$

Selfconsistency problem

* Initial estimate for $[N_{(-)}] \Rightarrow$ construct $[N_B]$, $[M_B]$ and $[V_{HF}]$.

* Solve s.p. eigenvalue problem $\Rightarrow$ QP energies $\epsilon_{Qj} = \lambda_j$ and orbitals $z_{Qj} = ([I] - [N_B\{N_{(-)}\}])u_j$

* N solutions with lowest energy are used to update density matrix

$$[N^{new}_{(-)}] = \sum_{i=1}^{N} z_{Qj} z^{\dagger}_{Qj} + [N_{B(-)}\{N_{(-)}\}]$$

* This closes selfconsistency loop, iterate to convergence.

* Energy can be obtained from

$$E^N_0 = \frac{1}{2}\sum_{j=1}^{N} z^{\dagger}_{Qj}([H_0] + \epsilon_{Qj}) z_{Qj}$$

$$+\frac{1}{2}\mathrm{Trace}([H_0][N_{B(-)}\{N_{(-)}\}] + [M_{B(-)}\{N_{(-)}\}])$$

Properties (1)

* QP-DFT generates total energy, density matrix and individual QP energies and orbitals, starting from a model for the background contributions as a functional of the density matrix.

* Reasonable strategy: external potential influences primarily QP part.

* Special case $[N_B] = 0$, $[M_B] = 0$ is equivalent to HF.

* Any KS-DFT model is also included as special case of QP-DFT with $[N_B] = 0$ and $[M_B]$ determined by E_{xc}.

* "Potentially exact" (or as exact as KS-DFT...)

Properties (2)

* For finite systems, the QP orbitals have the right asymptotics in coordinate space, provided the background operators are short-ranged.

* Can deal with soft Fermi surface (e.g. we checked that QP-DFT provides a correct description of H_2 dissociation in the spin-singlet state, eventhough it remains a s.p. description)

* Electron gas limit exists (see later).

How to model $[N_B]$ and $[M_B]$?

Building models for QP-DFT functionals

(1) Calculate spectral function in a series of test systems, using reasonable microscopic model for self-energy.
(2) Analyze QP-background separation.
(3) Parametrize background contribution to 0th and 1st moment.

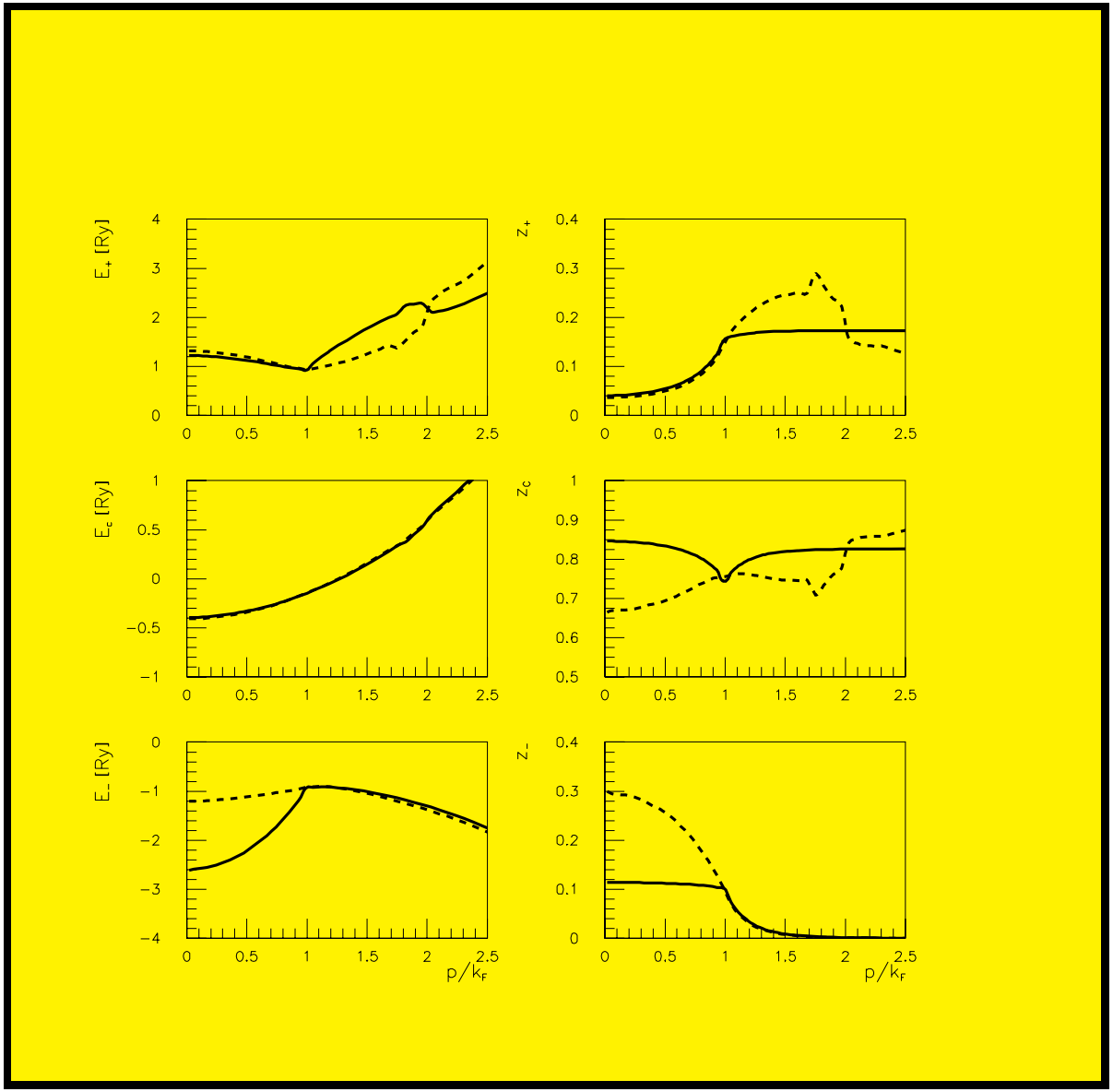
* Already experience with (1-2) through series of calculations using selfconsistent Green's function formalism, on light atoms [J.Chem.Phys. 115, 15 (2001);J.Chem.Phys. 117, 4095 (2002)], the electron gas [PRB 71, 245122 (2005)], and nuclear systems [PRL 90, 152501 (2003); PRC 68, 064307 (2003)].
* In each case QP-background separation was studied.
E.g.: electron gas results.

Electron gas in GW approximation

* GW = Self-energy including screening diagrams (coupling to plasmon), done selfconsistently (Hedin's equations).
Phys.Rev.B 71, 245122 (2005)

* QP-background separation was used to discretize the spectral function during the iterations towards a selfconsistent solution.

* Nice result: energy per particle is insensitive to precise prescription for QP-background separation, as long as sumrules are respected.



Background (+)

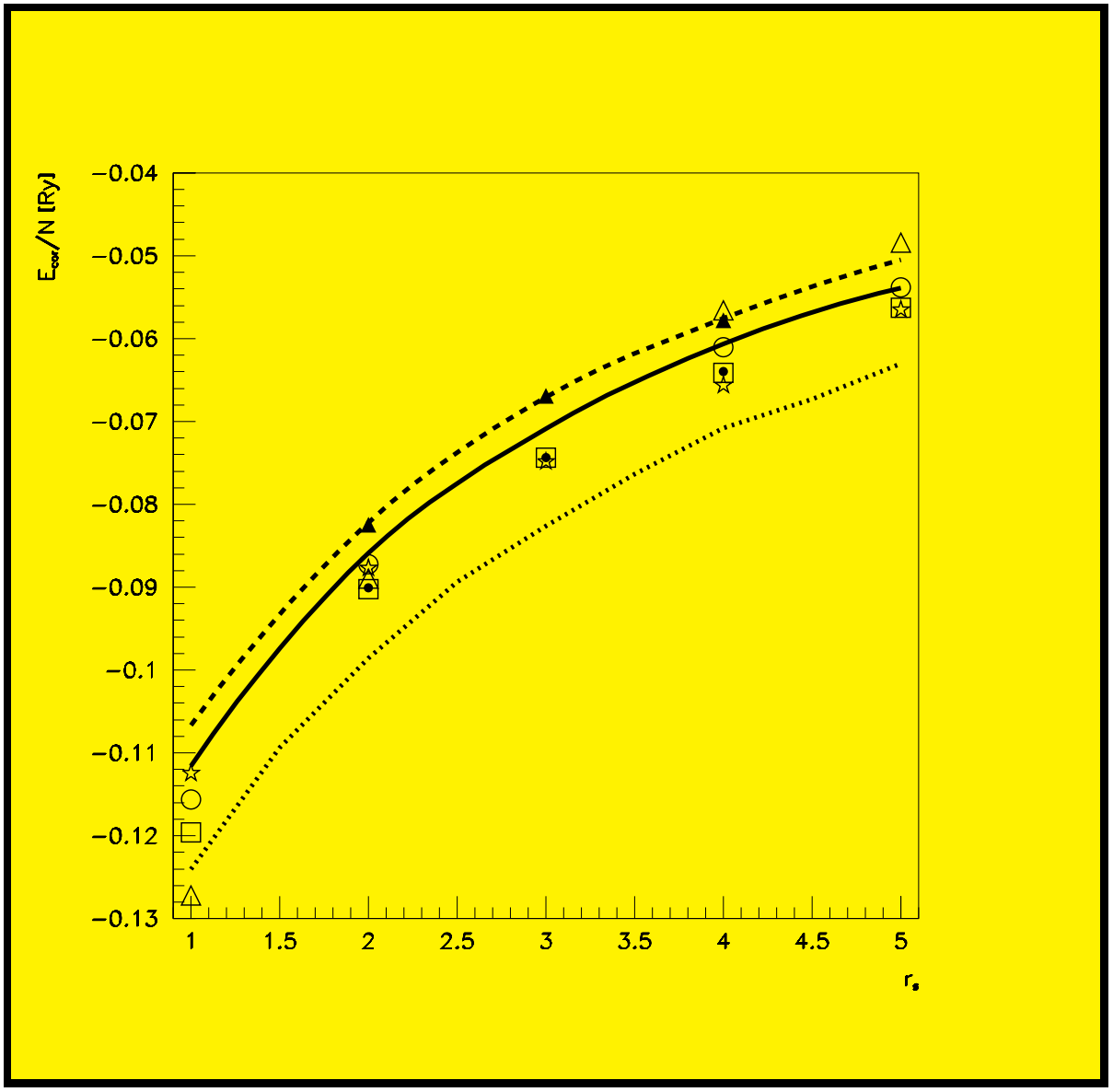
Quasiparticle

Background (-)

Energy

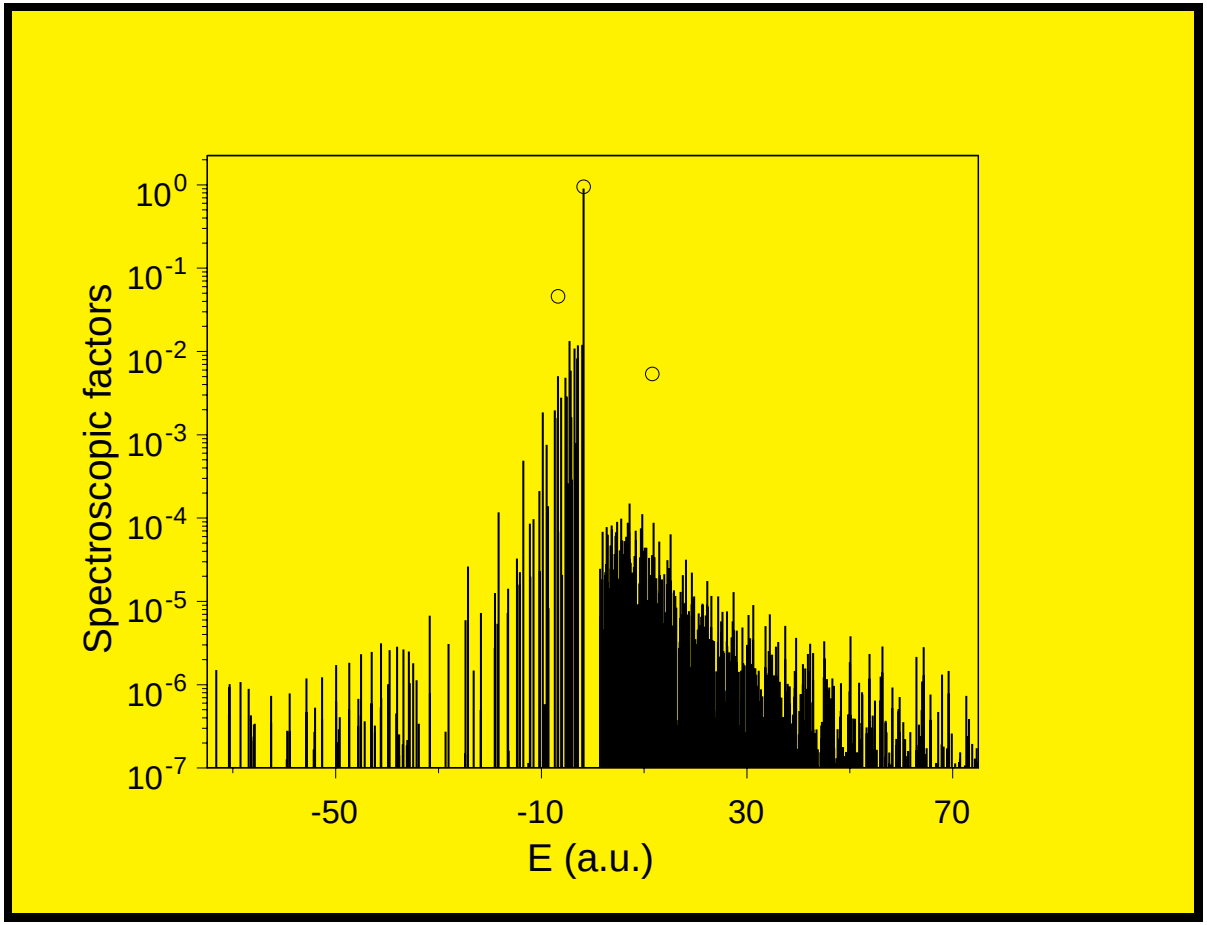
Strength

Energy per particle:

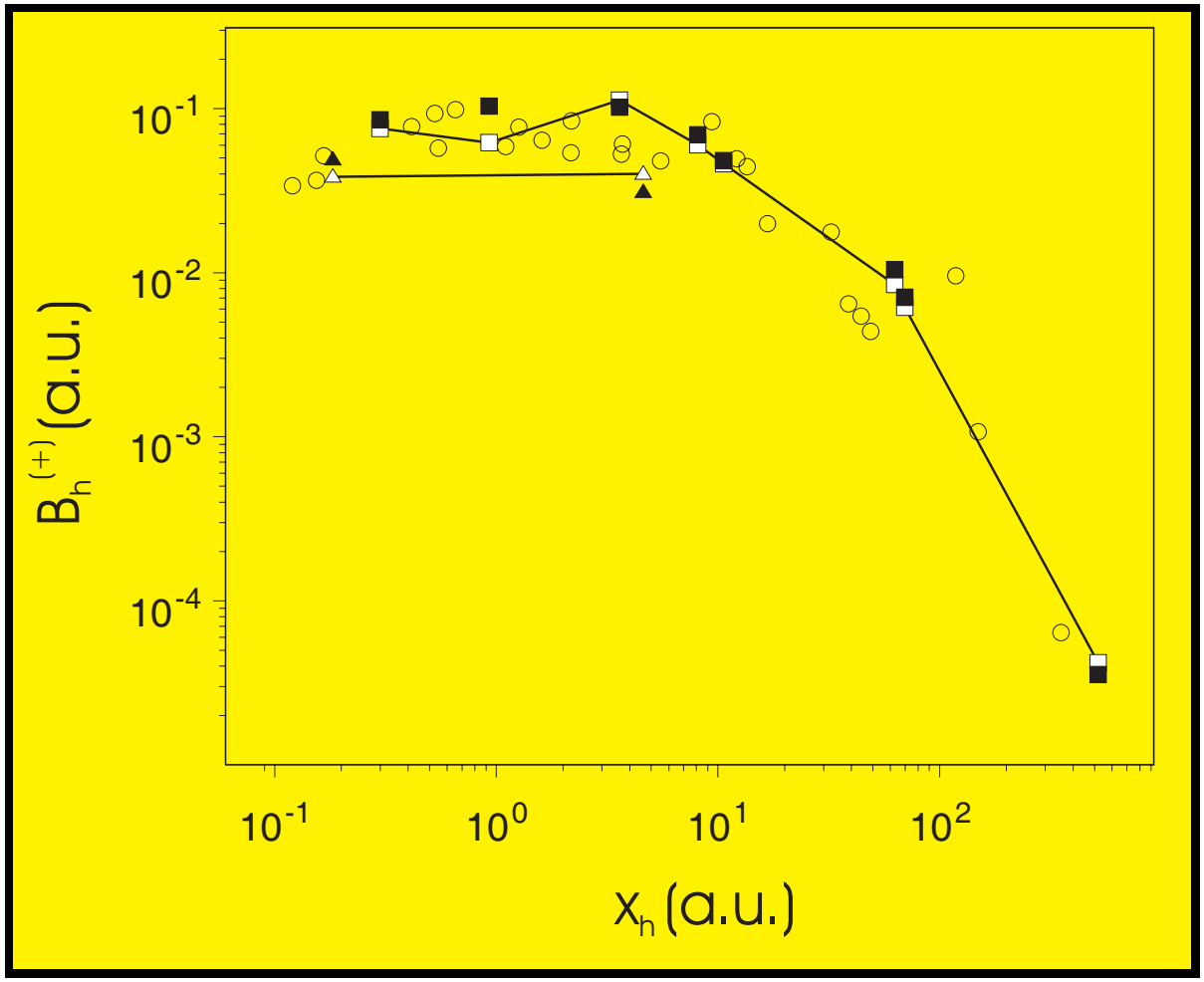


G_0W_0 approximation in closed-shell atoms

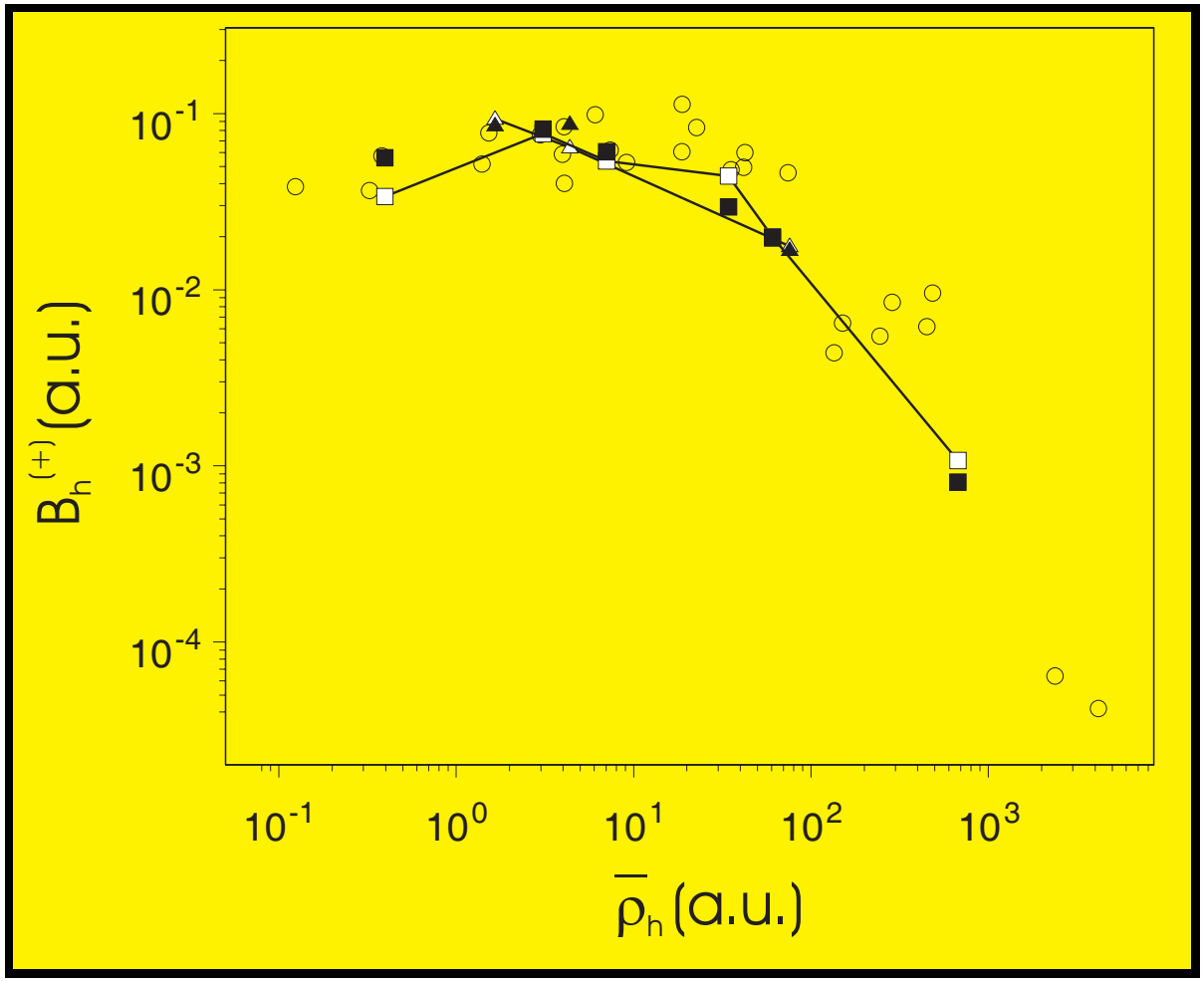
* Green's function calculation for He, Be, Ne, Mg, Ar, Ca, Zn, Kr, with self-energy at G_0W_0 level [PRA74, 062503 (2006)]
* QP-background separation for spectral function of 2s orbital in Ne



First moment of background addition strength $s_{Bh}^{(+)}(\epsilon_{Bh}^{(+)} - \epsilon_F)$ versus HF energy (relative to ϵ_F) for all hole orbitals in all atoms.



First moment of background addition strength $s_{Bh}^{(+)}(\epsilon_{Bh}^{(+)} - \epsilon_F)$ versus average density, for all hole orbitals in all atoms.



Construction of QP-DFT functional

* The background moments are not scattered randomly, but follow clear trends as a function of e.g. HF orbital energy / density.

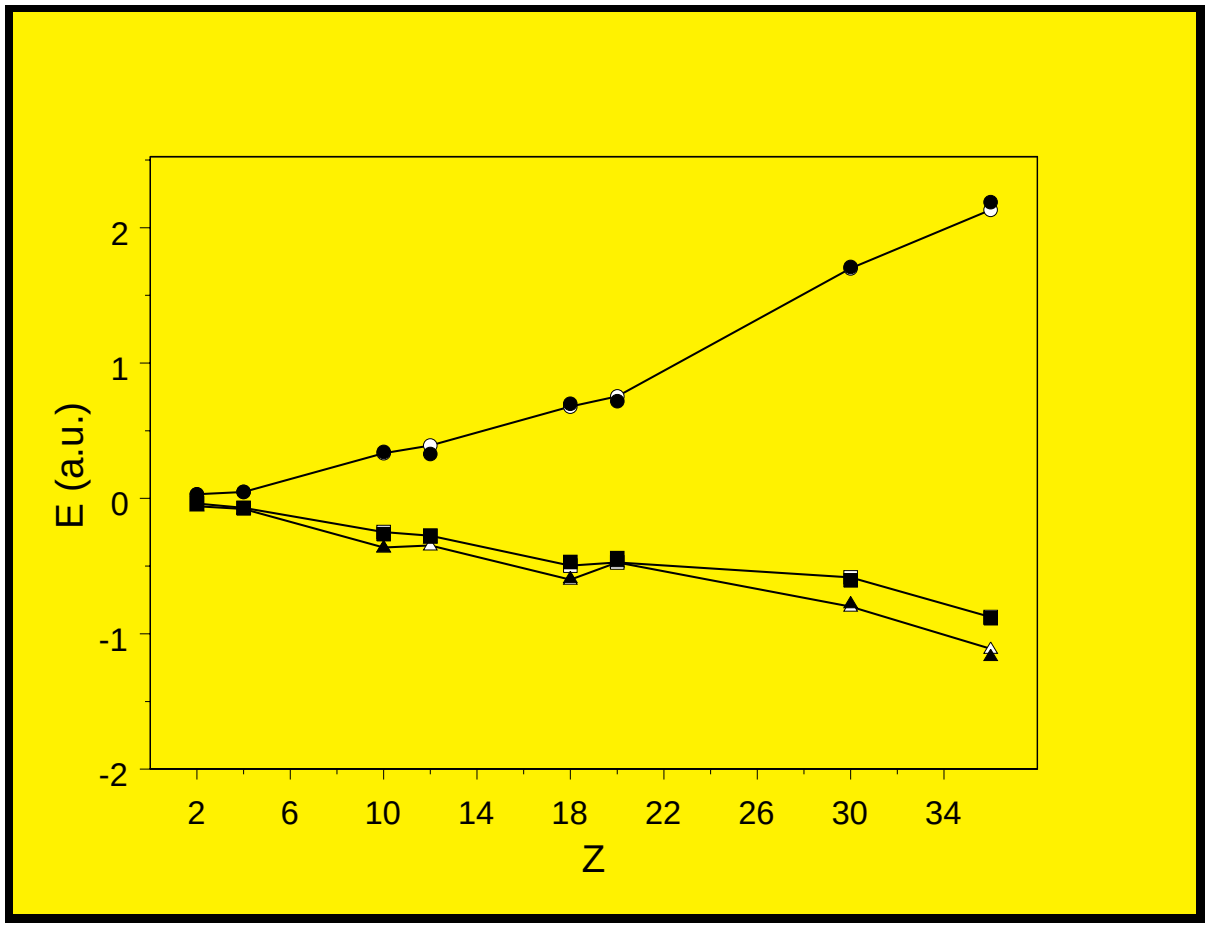
* This can be used to parametrize the background moments with a functional form. Additional variables to describe situation around Fermi energy: HF particle-hole gap, average density of ionization orbital.

* The resulting QP-DFT functional is able to reproduce the main results of the microscopic G_0W_0 calculation.

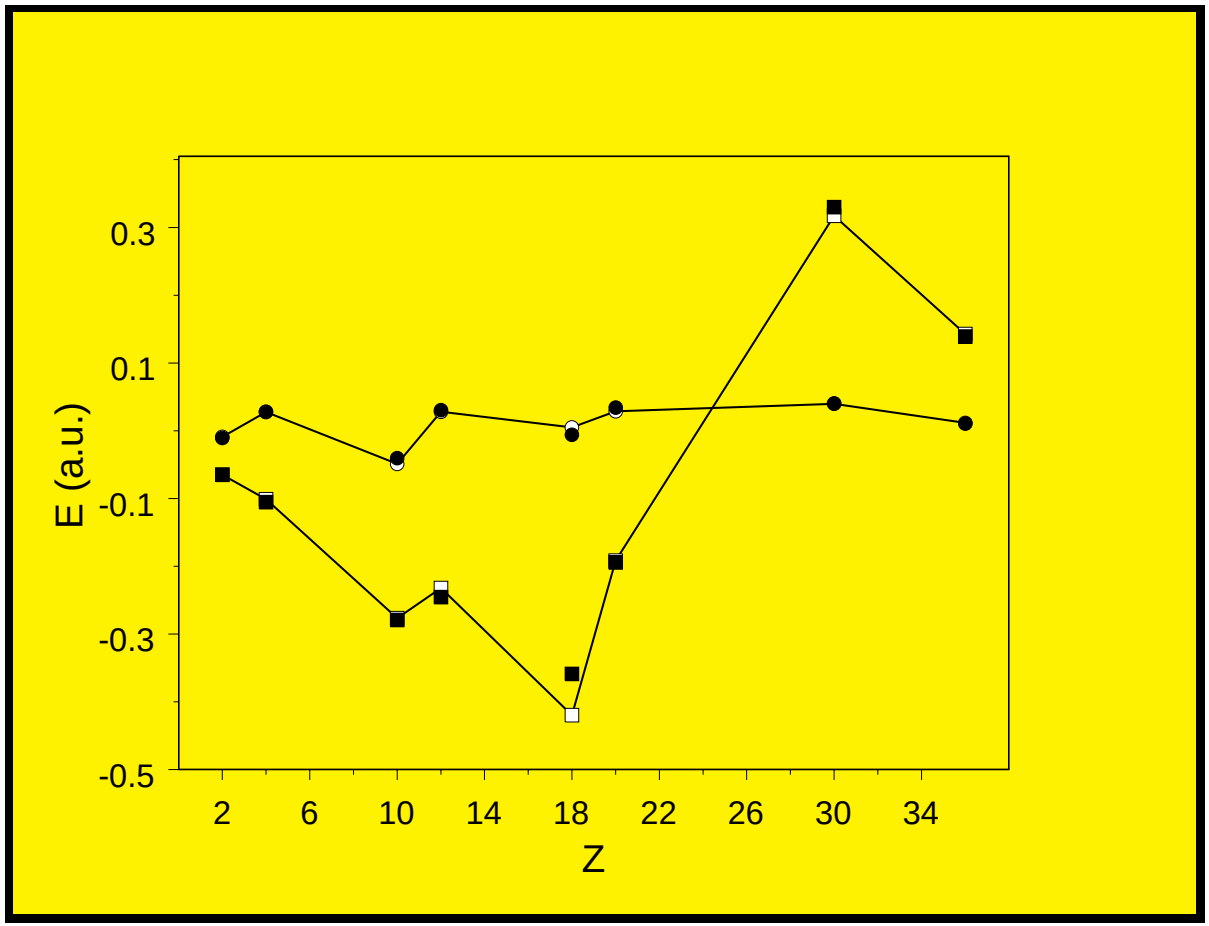
* Only proof-of-principle: not yet selfconsistent.

* Dependence on particle-hole gap is crucial.

Results of QP-DFT functional for separate contributions to the energy



Results of QP-DFT functional for total energy and ionization energy



Nuclear applications

* Nuclear DFT $\approx$ Skyrme Hartree-Fock parametrizations
* QP-DFT has extra degrees of freedom. More realistic model for nuclei as correlated systems, while keeping description at the s.p. level.
* What is the connection of QP-DFT with the dispersive optical model approach (Mahaux and co-workers) ?
* Modelling of self-energy, including energy-dependence, versus modelling of background contributions to the spectral function.
* Recent self-energy model for Ca isotopes [Charity,Sobotka,Dickhoff, PRL 97, 162503 (2006)] allows to study this in detail.

Summary

It is possible to derive DFT-like equations for QP orbitals.

A given QP-DFT functional yields predictions for the total energy and the density matrix of the system, as well as the QP orbitals, energies, and spectroscopic factors.

Finding suitable parametrizations for the background part in electronic systems is in progress.

Nuclear case: possibility of extending Skyrme mean-field models with terms that include explicit (short-range, long-range) correlation effects. More realistic description of nuclei at the s.p. level.