Correlation energy functional and potential from time-dependent exact-exchange theory.

Maria Hellgren

Ulf von Barth

Lund University

Contributors:

- C.-O. Almbladh
- F. Aryasetiawan
- N.E. Dahlen
- M. Hindgren
- S. Kurth
- R. van Leeuwen
- G. Stefanucci
- M. Stankowski

Within TDDFT the electronic linear density response function χ is given by

$$\chi = \chi_s + \chi_s(v + f_{\rm xc})\chi, \tag{1}$$

where χ_s is the Kohn-Sham (KS) linear density response function, v is the Coulomb interaction and $f_{\rm xc}$ is the XC kernel defined as the functional derivative of the XC potential $v_{\rm xc}$,

$$f_{\rm xc} = \frac{\delta v_{\rm xc}}{\delta n}. \tag{2}$$

Variational functionals

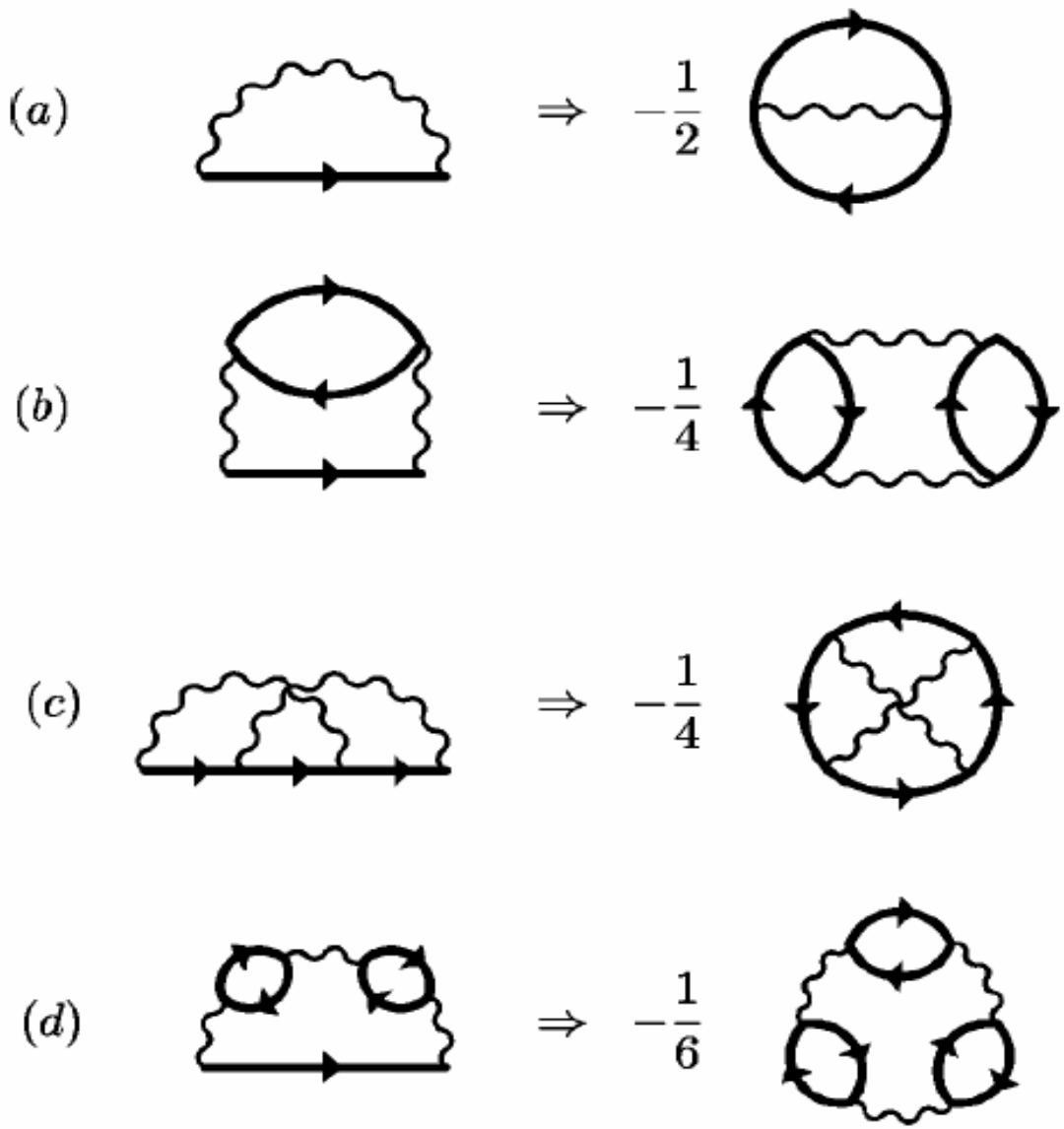
$$iY_{\mathrm{LW}}[G] = \Phi[G] - \mathrm{Tr}\{\Sigma G + \ln(\Sigma - G_{\mathrm{H}}^{-1})\} - iU_{\mathrm{H}}[G].$$

$$\Sigma = \frac{\delta \Phi}{\delta G}$$

$$D[G] = G(G_{\mathrm{H}}^{-1} - \Sigma[G]) - 1,$$

$$F[D=0] = \left(\frac{\delta F}{\delta D}\right)_{D=0} = 0,$$

Phi diagrams and self-energies



$$\Phi[G_s] = \frac{1}{2}\mathrm{Tr}\{\ln(1 + ivG_sG_s)\}.$$

Variational functionals cont.

$$F[D] = \mathrm{Tr}\{-D + \ln(D+1)\}$$

The Klein Functional

$$iY_K[G] = \Phi[G] - \mathrm{Tr}\{GG_H^{-1} - 1 + \ln(-G^{-1})\} - iU_o[G].$$

The Density Functional Trick: Vary only over Green functions produced by a local multiplicative potential

Klein Functional evaluated at a non-interacting Green function

$$Y_K[V] = -i\Phi[G_s] + T_s[n] + \int wn + U_0,$$

It is stationary when the potential generating G_s is

$$V = w + V_H - i\frac{\delta\Phi}{\delta n},$$

$$v_{xc} = -i\frac{\delta\Phi}{\delta n} = -i\int \frac{\delta\Phi}{\delta G_s}\frac{\delta G_s}{\delta V}\frac{\delta V}{\delta n}.$$

The restricted variation gives the linearized Sham-Schluter equation which is thus seen to be variational and not just perturbative!

$$\int \chi_s(1,2) v_{\rm xc}(2) d2 = \int \Sigma_s(2,3) \Lambda(3,2;1) d2 d3,$$

Here

$$i\Lambda(3,2;1) = \frac{\delta G_s(3,2)}{\delta V(1)} = G_s(3,1) G_s(1,2).$$

One more variation with respect to the total Kohn-Sham potential gives

$$\int \chi_s(1,2) f_{\mathrm{xc}}(2,3) \chi_s(3,4) d2d3$$

$$= \int \frac{\delta \Sigma_s(2,3)}{\delta V(4)} \Lambda(3,2;1) d2d3$$

$$+ \int \Lambda(1,2;4) \Delta(2,3) G_s(3,1) d2d3$$

$$+ \int G_s(1,2) \Delta(2,3) \Lambda(3,1;4) d2d3,$$

where

$$\Delta(2,3) = \Sigma_s(2,3) - v_{\mathrm{xc}}(2)\delta(2,3)$$

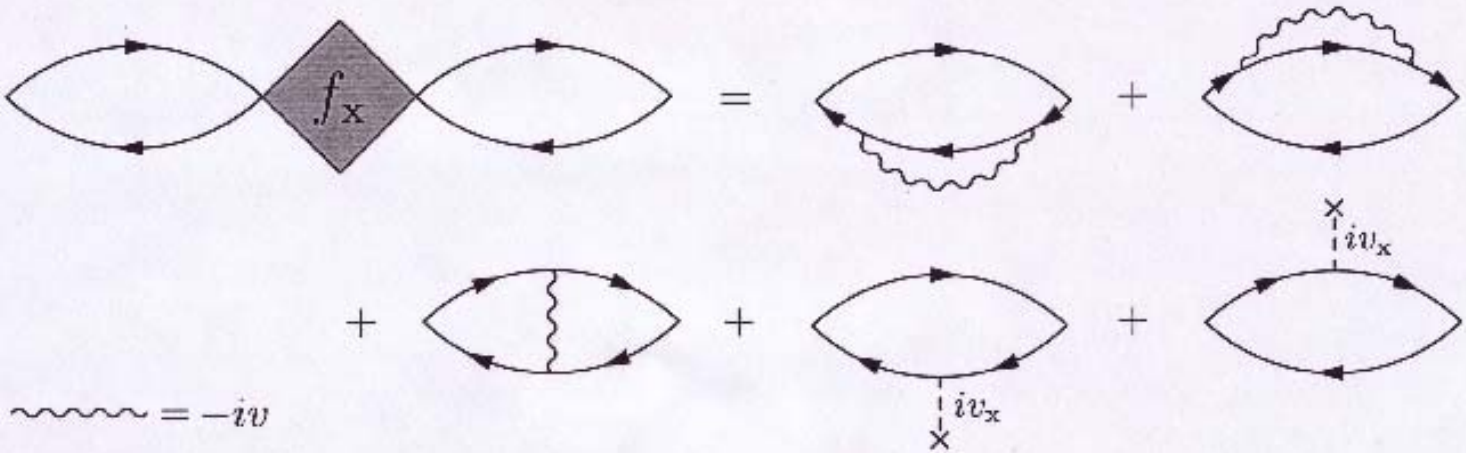
In the EXX approximation one chooses the Hartree-Fock diagram for the Φ functional

$$\Phi[G] = (i/2)\ \mathrm{Tr}[GGv]$$

leading to the HF self-energy

$$\Sigma[G] = i\ G\ v$$

Unfortunately, we now know that this procedure leads to a density response function with the wrong analytic structure.


f_x
=
+
+
+
+
iv_x
iv_x
$\sim\sim\sim\sim = -iv$

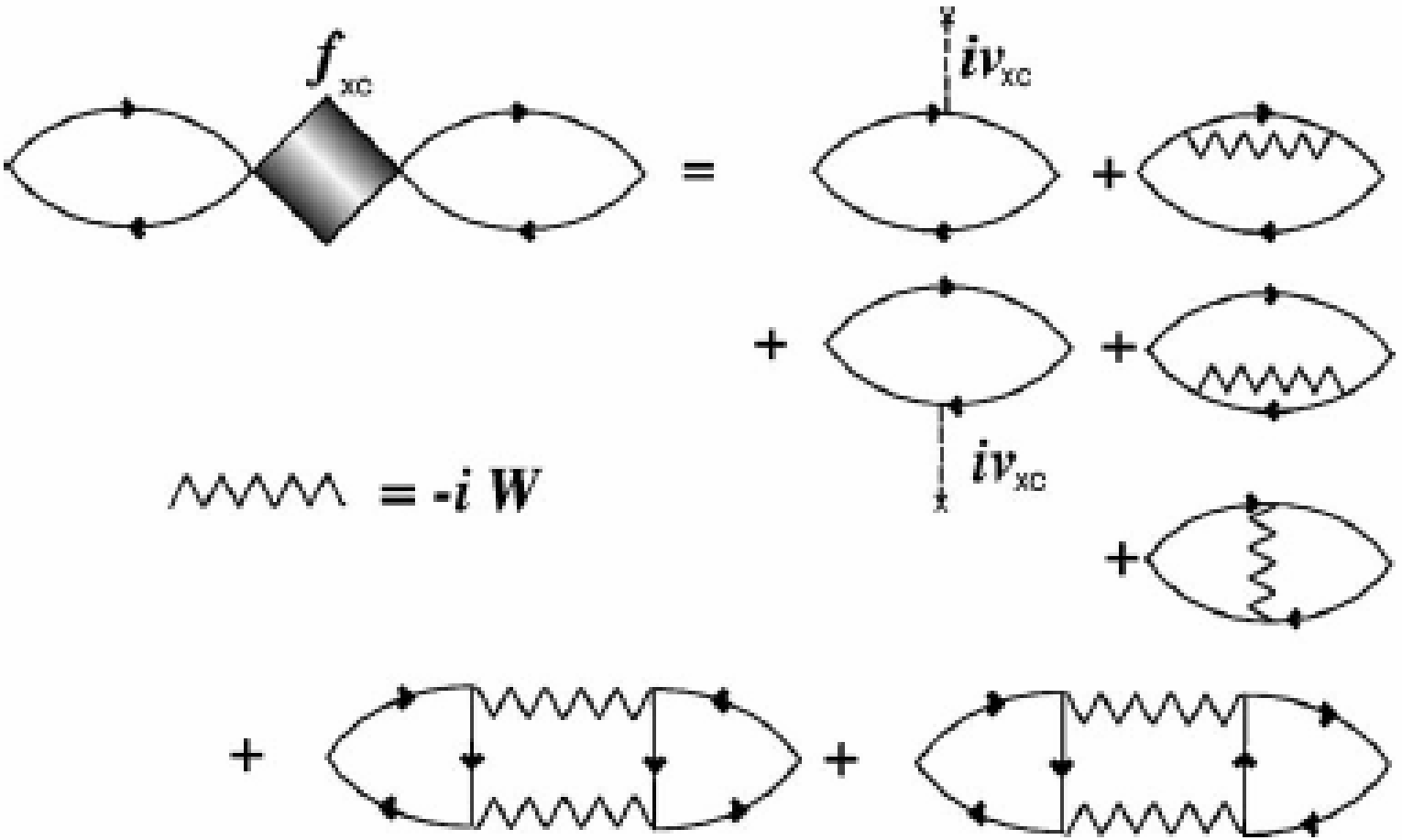
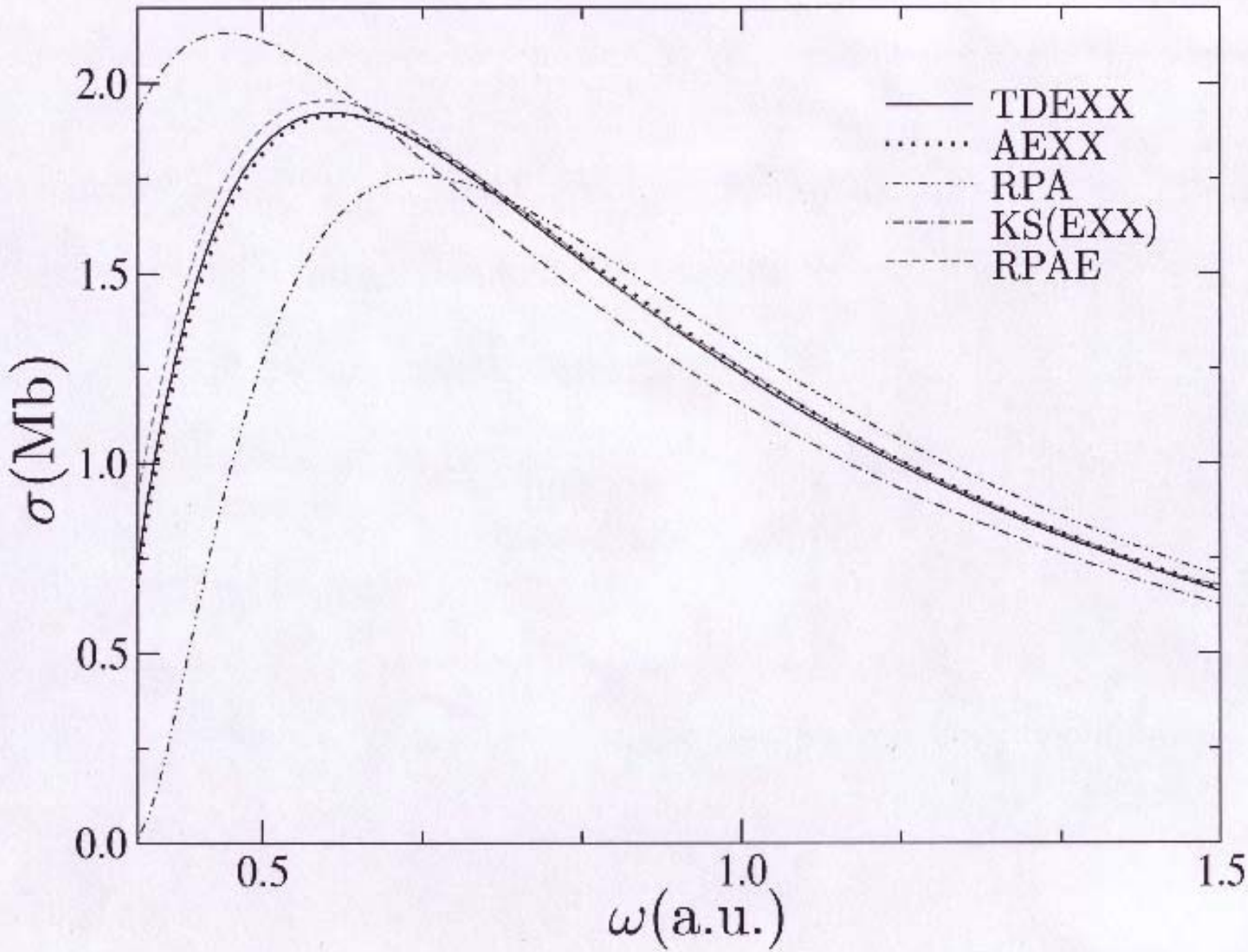

f_{xc}
=
iv_{xc}
+
+
+
iv_{xc}
+
+
$= -i\,W$

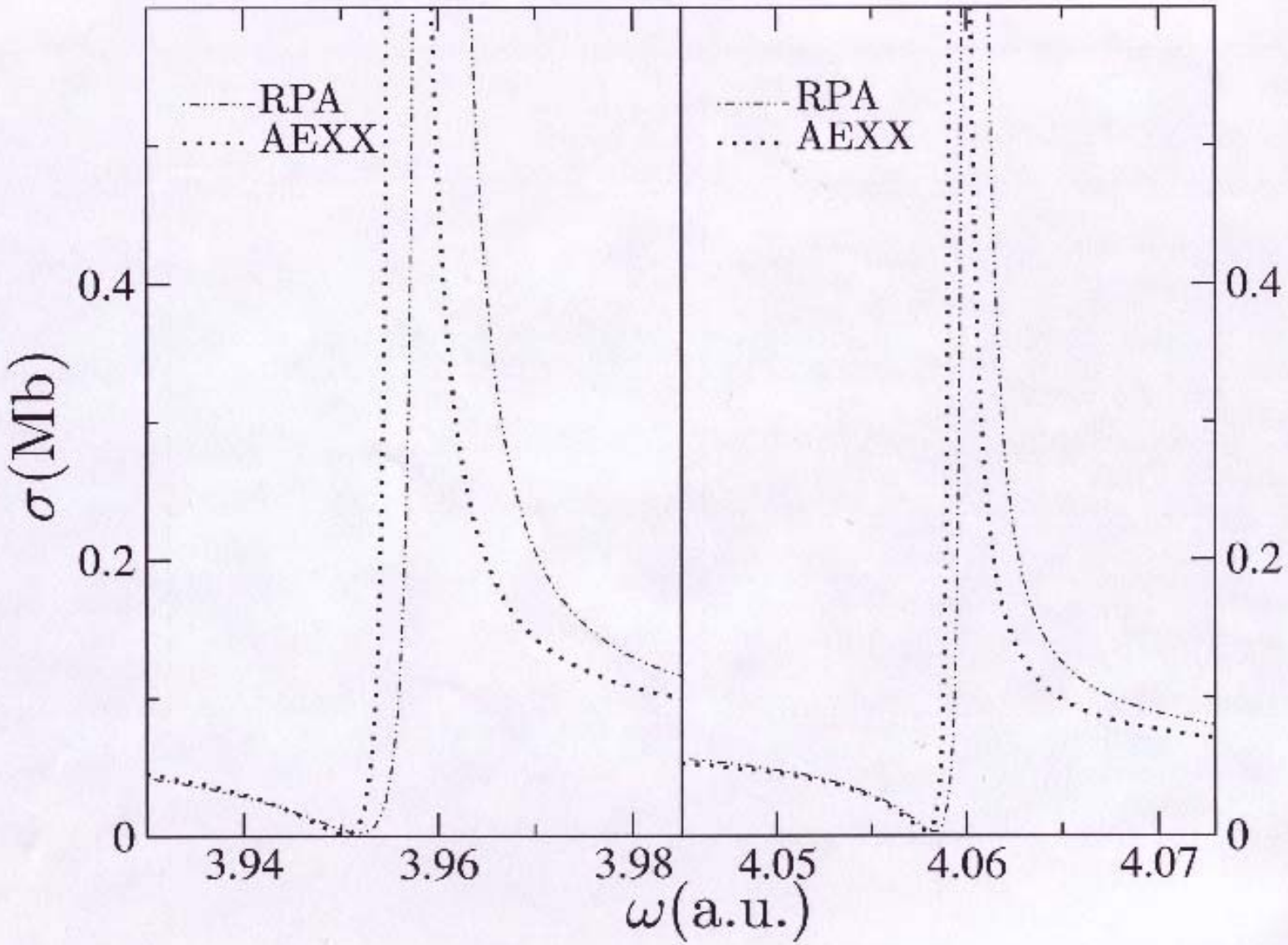
TABLE IV: The first few discrete excitation energies for Be and Ne in TDEXX compared to experimental, TDHF, RPA and KS transitions.

	Transition	KS	RPA	TDEXX	TDHF[a]	Exp.[b]
Be						
	2s→2p	0.1312	0.2032	0.1764	0.1764	0.1940
	2s→3p	0.2412	0.2547	0.2470	0.2471	0.2742
	2s→4p	0.2731	0.2777	0.2749	0.2750	0.3063
	2s→5p	0.2868	0.2889	0.2877	0.2878	0.3195
Ne						
	2p→3s	0.6585	0.6675	0.6803	0.6739	0.6190
	2p→4s	0.7793	0.7812	0.7827	0.7818	0.7268
	2p→5s	0.8134	0.8141	0.8147	0.8139	0.7593

[a]From Refs. 40,48.

[b]Adopted from Refs. 40,48.


TDEXX
AEXX
RPA
KS(EXX)
RPAE
σ(Mb)
ω(a.u.)
0.0
0.5
1.0
1.5
2.0
0.5
1.0
1.5


RPA
AEXX
RPA
AEXX
0.4
0.2
0
0.4
0.2
0
σ(Mb)
3.94
3.96
3.98
4.05
4.06
4.07
ω(a.u.)

But we can still obtain the total energy from the response function by applying the Hellman-Feynman theorem with respect to the strength of the Coulomb interaction

$$U_c = (i/2)\, \mathrm{Tr}[v \{ X - X_{KS} \}]$$

and

$$E_c = \int (d\lambda/\lambda)\, Uc$$

or, because f_x (EXX) is linear in the strength of the Coulomb interaction,

$$E_c = -(i/2)\, \mathrm{Tr}[\, v\, (v + f_x)^{-1}\, \ln\{1 - (v + f_x)\, X_{KS}\} + v X_{KS}\,]$$

Total energies of the electron gas (Hartree).

rs	RPA	ec2x	fxcorr	EC	Ceperly
1.00	-0.079	0.0242	-0.006	-0.061	-0.060
2.00	-0.062	0.0242	-0.008	-0.046	-0.045
3.00	-0.053	0.0242	-0.010	-0.038	-0.037
4.00	-0.047	0.0242	-0.011	-0.034	-0.032
5.00	-0.042	0.0242	-0.012	-0.030	-0.028
6.00	-0.039	0.0242	-0.013	-0.028	

TABLE I: Correlation energies from a few different approximations. For a consistent comparison with CI results the correlation energy is here defined as the difference between the total energy and the Hartree-Fock energy. Where necessary, a fourth decimal has been added in parentheses in order to compare different approximations. (a.u.)

f_{xc}:	TDEXX	AEXX	TDEXX	AEXX	RPA	MP2[b]	CI[c]
v_{xc}:	EXX	EXX	RPAX	RPAX	RPA	MP2	
He	0.044(5)	0.044(5)	0.044(6)	0.044(6)	0.083	0.047	0.0420
Be	0.102(0)	0.101(7)	0.103(3)	0.102(8)	0.181	0.124	0.0943
Ne	0.3889	0.377(1)	0.3903	0.377(8)	0.596	0.480	0.3905
Ar	0.7278	0.7106	0.7287	0.7112	1.091	0.844	0.7225

[b] From Ref. 16.
[c] From Ref. 17.

The Peuckert Iterative Procedure (1978)

- Start from any approximation to the exchange-correlation energy E_{xc} as a function of the strength of the Coulomb interaction.
- Form the derivatives $v_{xc} = \delta E_{xc}/\delta n$ and $f_{xc} = \delta v_{xc}/\delta n$.
- Calculate the linear density response function X from $X = X_o + X_o\,(v + f_{xc})\,X$.
- Calculate a new interaction energy U_{xc} from $U_{xc} = (i/2)\,\mathrm{Tr}[\,v\,X\,]$.
- Get a new exchange-correlation energy E_{xc} by integrating with respect to the Coulomb int. ….

In order to substantially simplify the calculations, two approximations have been made

- The energy dependence of the kernel f_x has been neglected.
- The density dependence of the f_x kernel has been neglected.
- These are NOT approximations for two-electron systems.

The equation for the RPA potential reads

$$X_{KS}\, v_{xc} = -2i\, G\, \Sigma_{GW}\, G\,, \quad \text{where}$$

$$\Sigma_{GW} = i\, G\, W = i\, G\, v\, (1 - v\, X_{KS})^{-1}$$

The equation for the RPAX potential reads

$$X_{KS}\, v_{xc} = -2i\, G\, \Sigma_{GG\Gamma}\, G\,, \quad \text{where}$$

$$\Sigma_{GG\Gamma} = i\, G\, W_{GG\Gamma} = i\, G\, v\, [1 - (v + f_x)\, X_{KS}]^{-1}$$

Notice that the same result could have been obtained as follows: knowing f_{xc} and thus χ from

$$\chi = \chi_{KS} + \chi_{KS} (v + f_{xc}) \chi$$

we can obtain the irreducible polarizability P from

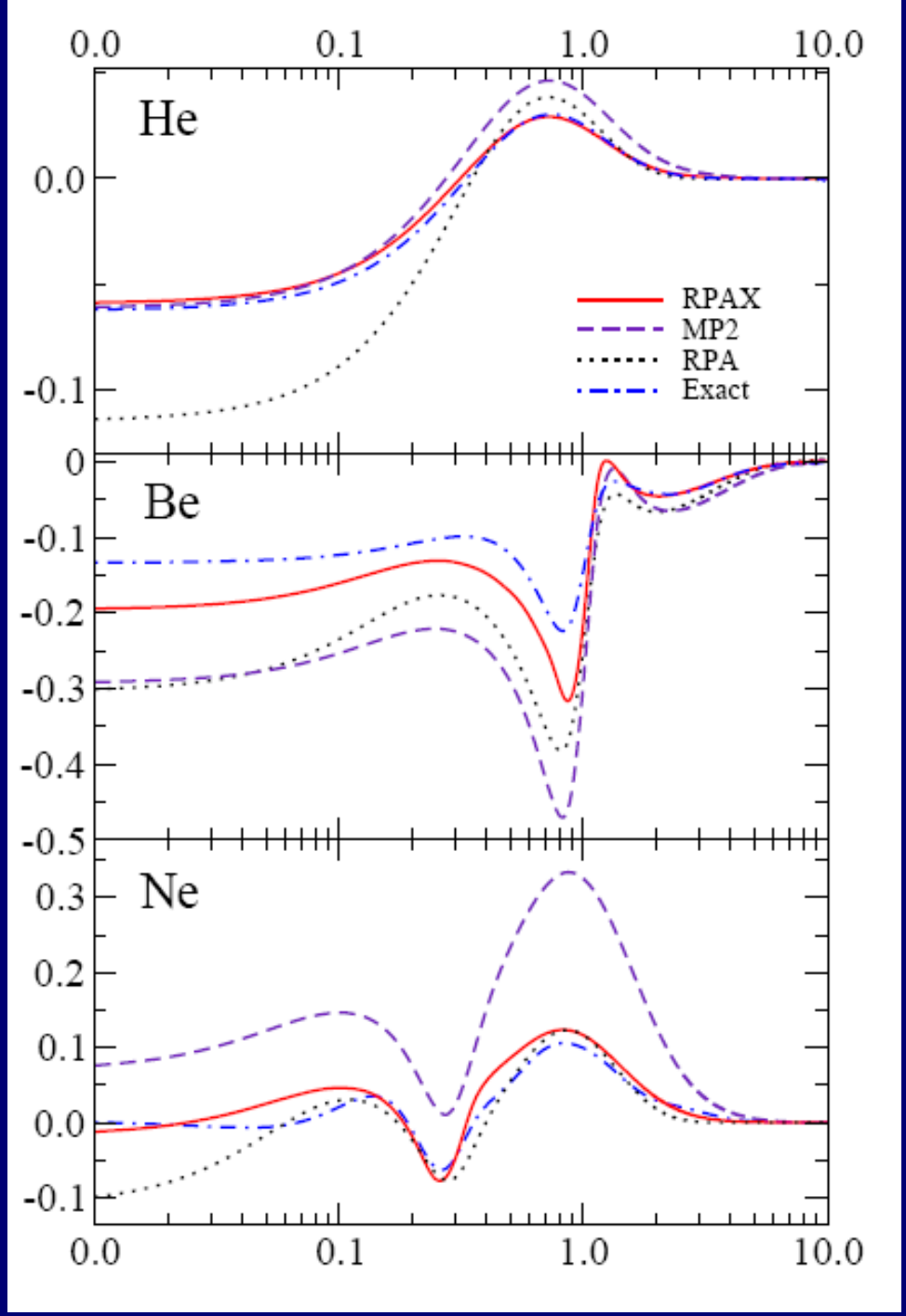
$$\chi = P + P v \chi$$

and an approximate local vertex Γ from

$$P = -i GG\Gamma$$

The exact expression for the self-energy then yields

$$\Sigma_{GGW} = i GW\Gamma = i G v [1 - (v + f_{xc}) \chi_{KS}]^{-1}$$



Correlation potentials for the atoms He, Be, and Ne.

MP2 is from Møller-Plesset perturbation theory – second order exchange processes.

Exact DFT potentials from Umrigar et. al.

TABLE II: Ionization potentials obtained from the highest occupied KS eigenvalue of different KS potentials. (a.u.)

Atom	EXX	MP2	RPA	RPAX	Exp.
He	0.918	0.893	0.902	0.904	0.904
Be	0.309	0.357	0.354	0.340	0.343
Ne	0.851	0.657	0.796	0.787	0.792
Mg	0.253	0.302	0.297	0.282	0.281
Ar	0.591	0.558	0.590	0.577	0.579

TABLE III: Static polarizabilities calculated from χ in the RPA and the TDEXX approximation. The latter has been evaluated using different potentials (EXX, RPA, RPAX, and Exact). (a.u.)

f_{xc}:	TDEXX				RPA	Litt.[a]
v_{xc}:	EXX	RPA	RPAX	Exact	RPA	
He	1.322	1.351	1.348	1.349	1.225	1.38
Ne	2.372	2.577	2.613	2.555	2.424	2.67
Ar	10.74	10.69	10.94	-	9.839	11.08
Be	45.64	40.09	41.04	40.49	28.99	37.8
Mg	81.66	70.37	71.67	-	51.56	71.53

[a]From Ref.[?]

TABLE IV: van der Waals or C_6 coefficients calculated from χ in the RPA, the AEXX and the TDEXX approximation. The latter has been evaluated using different potentials (EXX, RPA, RPAX, and Exact). (a.u.)

f_{xc}:	TDEXX				AEXX	RPA	Litt.
v_{xc}:	EXX	RPA	RPAX	Exact	RPAX	RPA	
He	1.375	1.414	1.411	1.411	1.411	1.206	1.458[a]
Ne	5.506	6.091	6.191	6.021	6.161	5.523	6.383[a]
Ar	61.88	61.27	63.19	-	63.11	53.69	64.3[a]
Be	282.8	226.7	235.3	231.5	236.5	142.0	214[b]
Mg	767.5	617.8		-	632.2	385.6	627[b]

[a]From Ref. 20.

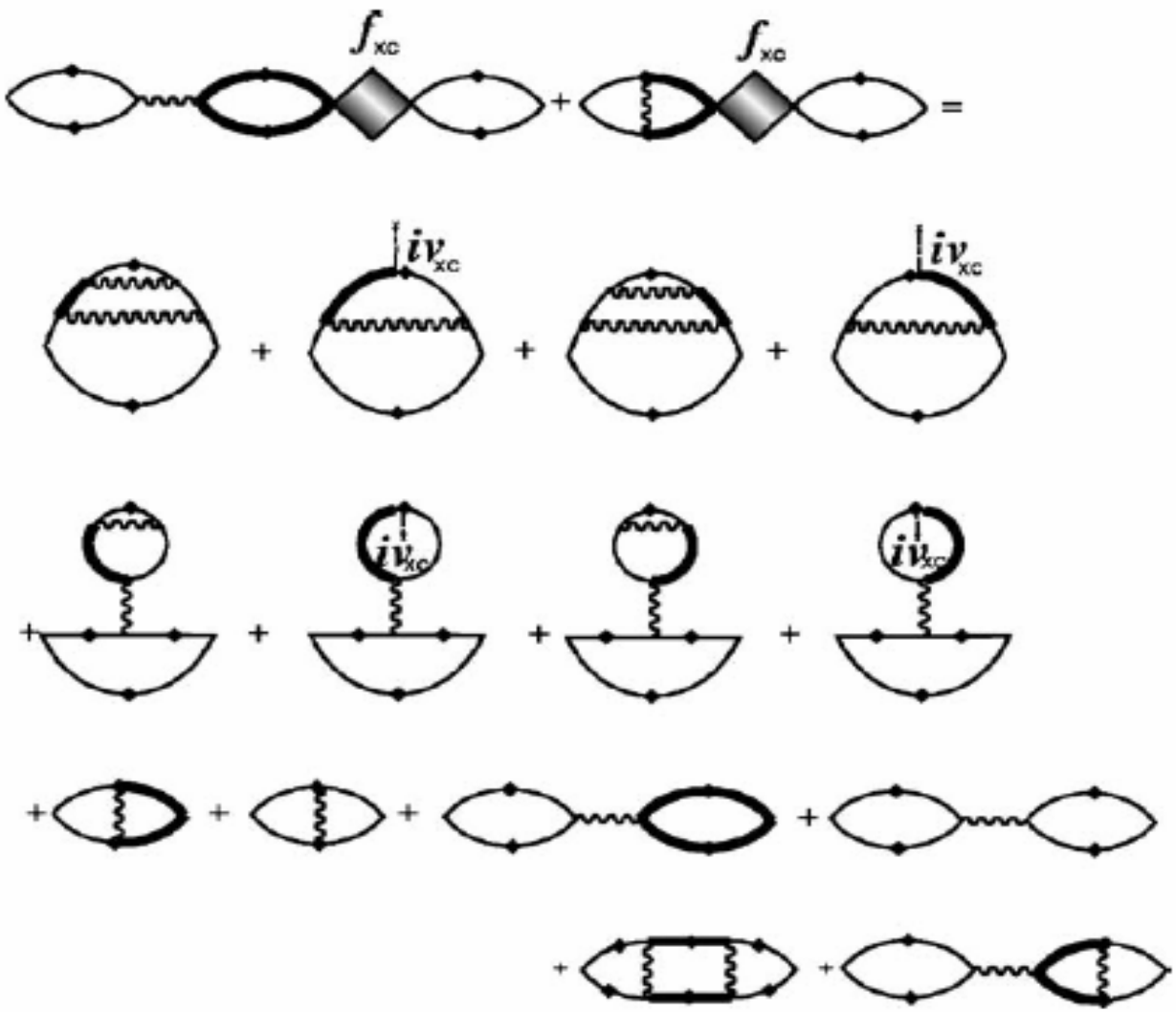
[b]From Ref. 21.

Conclusions

- The two major approximations have to be checked much more carefully in other systems.
- We now probably have the most accurate and feasible recipe for calculating an accurate Density Functional ground-state potential from which many important physical properties can be calculated with a high degree of accuracy.

- THANK YOU FOR YOUR ATTENTION!

The response function of the LW functional at the HF level



$$E_{\rm c} = \frac{i}{2}\int_0^1 d\lambda \int \frac{d\omega}{2\pi}\ {\rm Tr}\{v[\chi^\lambda(\omega) - \chi_s(\omega)]\}$$

$$\chi^\lambda = \chi_s + \chi_s\left[\lambda v + f_{\rm xc}^\lambda\right]\chi^\lambda$$

$$E_{\rm c} = -\frac{i}{2}\int \frac{d\omega}{2\pi}\ {\rm Tr}\left\{\ln[1 - v\chi_s] + v\chi_s\right\}$$

$$E_c = -\frac{i}{2}\int \frac{d\omega}{2\pi}\ {\rm Tr}\left\{\frac{v}{v + f_{\rm x}}\ln[1 - [v + f_{\rm x}]\,\chi_s] + v\chi_s\right\}$$