# ACFDT in a nutshell

For given density, n(r), we can define a family of Hamiltonians,  $\hat{H}_{\lambda}$ , with electron-electron repulsion scaled by a factor  $\lambda$  and an external potential,  $V^{\lambda}$ , such that the density remains unchanged:

$$\hat{H}_{\lambda} = \hat{T} + \lambda \hat{W} + \int V^{\lambda}(r)\hat{n}(r)dr.$$
(1)

This allows to define corresponding HK functionals, via Levy's constrained search if necessary, as

$$F_{\lambda}[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \lambda \hat{W} | \Psi \rangle = T_{\lambda}[n] + \lambda W_{\lambda}[n], \qquad (2)$$

with obvious meaning of the kinetic-energy and Coulomb interaction contributions as the expectation values of the corresponding operators on the  $\lambda$ -dependent GS wavefunction,  $\Psi_{GS}^{\lambda}(r_1, r_2, ..., r_N)$  (spin-dependence and/or density-matrix character integrated out for the time being).

In particular one can define the density

$$n(r) = N \int dr_2 dr_3 \dots dr_N |\Psi_{GS}^{\lambda}(r, r_2, r_3, \dots r_N)|^2,$$
(3)

and the 2-particle distribution function

$$n_{\lambda}^{(2)}(r,r') = N(N-1) \int dr_3 ... dr_N |\Psi_{GS}^{\lambda}(r,r',r_3,...r_N)|^2,$$
(4)

such that the scaled Coulomb interaction  $W_{\lambda}[n]$  can be expressed as

$$W_{\lambda}[n] = \frac{e^2}{2} \int dr dr' \frac{n_{\lambda}^{(2)}(r,r')}{|r-r'|}.$$
(5)

The  $F_{\lambda}$  functionals are variational w.r.t. (neutral) density variations, hence:

$$\frac{dF_{\lambda}}{d\lambda} = F_{\lambda}' = W_{\lambda}, \qquad T_{\lambda}' + \lambda W_{\lambda}' = 0, \qquad T_{\lambda}'' + \lambda W_{\lambda}'' > 0, \tag{6}$$

where the last inequality stems from the fact that each  $F_{\lambda}$  is a minimum w.r.t to density. Taking a further derivative of the above second equality one obtains

$$T_{\lambda}^{\prime\prime} + \lambda W_{\lambda}^{\prime\prime} + \lambda W_{\lambda}^{\prime} = 0 \implies W_{\lambda}^{\prime} < 0.$$
<sup>(7)</sup>

Hence the positive definite Coulomb interaction energy monotonically decreases from the Hartree+Exchange value for  $\lambda = 0$  to the Strictly Correlated Electron (SCE) value for  $\lambda = \infty$ ; the physical  $\lambda = 1$  case being in between.

The physical HK functional then becomes

$$F[n] = F_1[n] = F_0[n] + \int_0^1 d\lambda W_\lambda[n] = T_s[n] + E_H[n] + E_{xc}[n]$$
(8)

where it is convenient, or maybe just conventional, to isolate the direct (Hartree) Coulomb interaction that does not depend on  $\lambda$  since so does the density,

$$E_H[n] = U[n] = \frac{e^2}{2} \int dr dr' \frac{n(r)n(r')}{|r-r|}, \qquad E_{xc}[n] = \int_0^1 d\lambda W_\lambda[n] - U[n]. \tag{9}$$

Let us define the Exchange energy from  $W_{\lambda}$  in the limit of vanishing interaction:  $E_x[n] = W_0[n] - U[n]$ . Correlation is therefore defined as

$$E_c[n] = \int_0^1 d\lambda \left( W_\lambda[n] - W_0[n] \right) = \int_0^1 d\lambda \left( \langle \Psi_{GS}^\lambda | \hat{W} | \Psi_{GS}^\lambda \rangle - \langle \Psi_{GS}^0 | \hat{W} | \Psi_{GS}^0 \rangle \right).$$
(10)

We can play with the second-quantization definition of the interaction

$$\hat{W} = \frac{1}{2} \int dx dy \frac{\phi^{\dagger}(x)\phi^{\dagger}(y)\phi(y)\phi(x)}{|x-y|} = \frac{1}{2} \int dx dy \frac{\hat{n}(x)\hat{n}(y)}{|x-y|} - \frac{\hat{N}}{2}v_c(0),$$
(11)

where the last term is divergent but since the number of electrons does not change while variing  $\lambda$  it cancels exactly in taking the difference,

$$E_{c}[n] = \frac{1}{2} \int_{0}^{1} d\lambda \int dr dr' \left\{ v_{c}(r-r') \left[ \langle \Psi_{GS}^{\lambda} | \hat{n}(r) \hat{n}(r') | \Psi_{GS}^{\lambda} \rangle - \langle \Psi_{GS}^{0} | \hat{n}(r) \hat{n}(r') | \Psi_{GS}^{0} \rangle \right] \right\}.$$
(12)

We can then insert a resolution of the identity and play with the basic integral  $\int_0^\infty \frac{1}{1^2+x^2} dx = \pi$  and the possible electronic transitions to transform it in the FD formula

$$E_c[n] = -\frac{\hbar}{2\pi} \int_0^1 d\lambda \int_0^\infty du Tr\left\{v_c\left[\chi^\lambda(iu) - \chi^0(iu)\right\}\right\}.$$
(13)

**NB:** These steps require some further analysis, especially in the degenerate case since the excluded GS term is not anymore the Hartree energy and therefore does not cancel exactly.

The basic ingredient becomes then the (imaginary-)frequency density-density response function, whose expansion in powers of  $\lambda$  can be obtained from perturbation theory. It is convenient to express this dependence via a Dyson-like equation, which amounts to take a Taylor expansion of the inverse of the response function,

$$\chi_{\lambda}(iu) = \chi_0(iu) + \chi_0(iu)(\lambda v_c + f_{xc}^{\lambda})\chi_{\lambda}(iu) \quad \Longleftrightarrow \quad \chi_{\lambda}^{-1}(iu) = \chi_0^{-1}(iu) - (\lambda v_c + f_{xc}^{\lambda}) \tag{14}$$

where each term in the xc kernel can be obtained from perturbation theory of appropriate order.

Nice and clean but high-order perturbative expansion is in general tedious and cumbersome and the desired value of  $\lambda$  may well be outside its convergence radius. Truncation can introduce other problems, as for instance the case of RPAx (linear term in  $f_{xc}$ ) that becomes unstable in the low density limit in the HEG and probably in general.

Some kind of analytical continuation or interpolation, to extend the domain of applicability of the expansion and avoid diverging solutions, may be desirable.

### from Perturbation Theory to Interaction Strenght Interpolation

Since the  $\lambda = 0$  KS case is the one system that we are able to compute exactly it is natural to start from there and epxlore the behavior of the functional as  $\lambda$  is switched on,

$$W_{\lambda} = W_0 + W'_0 \lambda + \dots, \qquad \lambda \sim 0. \tag{15}$$

The  $W_0[n]$  term is the expectation value of the interaction evaluated on the KS state. It corresponds to the Hartree energy (see above) and the Fock Exchange energy, evaluated with the KS orbitals:

$$E_x = -\frac{e^2}{2} \int dr dr' \sum_{\sigma} \sum_{i,j} \frac{\rho_{\sigma i,j}(r) \ \rho^*_{\sigma i,j}(r')}{|r - r'|}, \qquad \rho_{\sigma i,j}(r) = \varphi^*_{\sigma i}(r)\varphi_{\sigma j}(r). \tag{16}$$

The linear term in the interaction strength is (twice) the second-order term in the Goerling-Levy perturbation expansion  $W'_0[n] = 2E^{(2)}_{GL}$  and can be calculated exactly in the ACFDT formalism at the RPAx level.

In the strongly interacting limit,  $\lambda \to \infty$ , the dependence is instead

$$W_{\lambda} = W_{\infty} + W_{\infty}'/\sqrt{\lambda} + W_{\infty}''/\lambda + \dots, \qquad \lambda \to \infty, \tag{17}$$

where  $W_{\infty} = \lim_{\lambda \to \infty} W_{\lambda}$ ,  $W'_{\infty} = \lim_{\lambda \to \infty} \sqrt{\lambda} (W_{\lambda} - W_{\infty})$  and  $W''_{\infty}$  can be shown to vanish identically.

In the  $\lambda \to \infty$  limit the electrons become strictly correlated in the sense that their wavefunction squared becomes a superposition of product of delta functions where electrons are localized in correlated positions defined by "co-motion" functions such that as one electron moves the other adjust their positions to minimize the electrostatic energy while on average keeping the prescribed density. The wavefunction can be described as a kind of floating Wigner crystal and the corresponding minimization problem becomes essentially classical.

Indeed sending  $\lambda \to \infty$  is equivalent to sending  $\hbar^2$  in the kinetic energy to zero. Since in the semiclassical expansion the "small" parameter is  $\hbar$ , in the large  $\lambda$  regime the proper expansion parameter is  $1/\sqrt{\lambda}$ . This can be seen independently considering that the first non-constant term in the expansion is associated to the zero-point vibrational energy of electrons around their classical minima in the floating Wigner crystal (proportional to  $\hbar\omega$ , where  $\omega^2 \sim K/m\lambda$ ).

The Interaction Strenght Interpolation (ISI) approach introduces an interpolation between the two limits that satisfies these conditions exactly or at least approximately when this is not possible. More than one form has been proposed and there is some arbitrariness. There are coordinate-scaling relationships for  $W_{\lambda}[n]$  (see later) that can be used to limit somehow this arbitrariness, but do not count too much on these, typically they are trivial to satisfy.

Another (approximate) way to constrain the interpolation is to reproduce the small  $\lambda$  expansion up to a given power of a given approximation thought to be accurate. For instance, considering RPAx, that is exact only to the linear order in  $\lambda$  but via the Dyson equation is defined at every order, one could calculate higher (quadratic, cubic, ...) orders and force the interpolation to reproduce them in addition to the large  $\lambda$ behavior. In this way for systems where the convergence radius of the expansion is larger than 1, and RPAx is probably accurate, its behavior can be recovered. I don't know whether this is a good idea. My feeling is that the  $\lambda$  dependence in  $W_{\lambda}$  should be relatively dull and too much tweeking might introduce instabilities rather than cure them. One could probably compare the approximate  $W_{\lambda}$  otained from RPAx, ISI, and the combination of the two for a few systems and see how they perform.

### size consistency and the need for LIISA

In the original ISI approach the interpolation is performed between system-integrated quantities, obtaining in this way encouraging results. However interpolation of global quantites cannot be size consistent (that is the energy of A+B would not in general be the energy of A + the energy of B) unless the interpolation ingredients enter olny linearly, which is not what have been proposed so far and is kind of awkward because then the switching value between the two limits would not depend on the system but be somewhat universal, which appears unlikely.

Another possibility is to define the ISI on top of some range separation, that would split the integral in disjoint pieces. I don't know exactly and I don't like it because again this range separation appears artificial while it should emerge naturally from the properties of the system.

A viable solution is to define a position-dependent xc energy *density* and interpolate it. With this Locally Interpolated Interaction Strenght Approximation (LIISA) size consistency is automatic if the energy density depends on the local (in a broad sense) properties of the system.

There is however some arbitrariness in the definition of the xc energy density since the interaction is by definition non local and the xc energy is a system-integrated quantity, so it is not so clear how to define it.

# a physically motivated exchange-correlation energy density definition

One prescription that is often (always?) found in the literature defines the energy density at a given point r in terms of the interaction energy of an electron located there with the (coupling constant averaged) xc hole it generates around itself. Looks nice and people are drawn to this definition by the sum-rule that the xc-hole satisfies and could be used to constraint the functional form, but the role of r and r' in the defining integrals is very symmetric and I see no reason to focus on only one of the two. Applying the same approach to the Hartree term one would identify the Hartree energy density with half the Hartee potential which is not what J.C. Maxwell teaches us.

Actually, for a classical distribution of charges the electrostatic interaction energy can be defined as the integral of an energy density defined as

$$w_H(r) = \frac{1}{8\pi} |E(r)|^2.$$
 (18)

It is quite natural to generalize this results to the exchange term as

$$w_x(r) = -\frac{1}{8\pi} \sum_{\sigma} \sum_{i,j} |E_{\sigma i,j}(r)|^2,$$
(19)

where  $E_{\sigma i,j}(r)$  is the electric field generated by the auxiliary charge distribution  $\rho_{\sigma i,j}(r)$  previously defined. It is easy to see that  $w_x(r)$  is invariant for unitary transformations among the orbitals in the occupied manyfold.

More in general we can use the following basic electrostatic identity

$$\frac{1}{|r'-r''|} = \frac{1}{4\pi} \int dr \nabla \left(\frac{1}{|r-r'|}\right) \cdot \nabla \left(\frac{1}{|r-r''|}\right),\tag{20}$$

(that is most easily demonstarted by feeding the Fourier transform representation of the Coulomb kernel) to get the following expression

$$w_{\lambda}(r) = \frac{1}{8\pi} \int dr' dr'' \nabla \left(\frac{1}{|r-r'|}\right) \cdot \nabla \left(\frac{1}{|r-r''|}\right) n_{\lambda}^{(2)}(r',r'')$$
(21)

that for  $\lambda = 0$  reduces to  $w_0(r) = w_H(r) + w_x(r)$ .

For general  $\lambda$  we can use the ACFDT expression in terms of the response function to define

$$w_c(r) = -\frac{\hbar}{2\pi} \int_0^1 d\lambda \int_0^\infty du \int dr' dr'' \nabla \left(\frac{1}{|r-r'|}\right) \cdot \nabla \left(\frac{1}{|r-r'|}\right) \left[\chi^\lambda(r',r'',iu) - \chi^0(r',r'',iu)\right]. \tag{22}$$

The term inside the integral is the (imaginary-)frequency-dependent electric field induced at the position r by the response of the system to an oscillating elemental dipole in r. It looks very much like a classical FD results except that the eigenmodes being excited are the ones of the quantum system.

## Stricly Correlated Electrons from (quantum) Langevin dynamics

The  $\lambda \to \infty$  strictly correlated electrons (SCE) system is a quite pathological one when seen as a quantum system but we can think of it as a system of classical charges at a small finite temperature in an external potential such that the average density is as desired. All is needed is a way to sample the canonical distribution at a conveniently low temperature. Langevin dynamics is a possible methods for this and

there is also the option of using colored noise to sample the harmonic excitations according to quantum statistics thus giving access to the ZPE  $W'_{\infty}$  term as well.

$$W_{\lambda}^{cl}[n] = \langle \langle \frac{e^2}{2} \sum_{\substack{i,j \\ i \neq j}} \frac{1}{|r_i - r_j|} \rangle \rangle_{\lambda}$$
(23)

where  $\langle \langle ... \rangle \rangle_{\lambda}$  means the statistical average over the distribution associated to a given value of  $\lambda$ . I dont know the details but I would say the classical result should correspond to  $\lambda = \infty$  while a finite "quantum" result should give access to ZPE.

**NB**: It should be possible to test the approach on unidimensional systems where the SCE equation can be solved numerically in another way.

When an interaction energy density is desired one should use the classical expression

$$w_{\lambda}^{cl}(r) = \langle \langle \frac{1}{8\pi} \sum_{\substack{i,j\\i \neq j}} E_i(r) \cdot E_j(r) \rangle \rangle_{\lambda}$$
(24)

where  $E_i(r)$  is the electric field generated in r by particle i, possibly smoothed for a finite size set in such a way that two different electrons never overlap (due to Gauss theorem the integrated interaction energy should not depend on that).

#### about scaling relationship for the energy and the energy density

Coordinate scaling can be used to connect functionals values at different interaction strength. It is relatively easy to see that if  $\Psi(r_1, r_2, ..., r_N)$  is a solution corresponding to density n(r) for the physical  $\lambda = 1$  interaction strength, then  $\Psi_{\gamma}(r_1, ..., r_N) = \gamma^{3N/2} \Psi(\gamma r_1, ..., \gamma r_N)$ , corresponding to density  $n_{\gamma}(r) = \gamma^3 n(\gamma r)$ , is a solution for the Hamiltonian with scaled interaction strength  $\lambda = \gamma$  with energy and energy components linked as

$$E_{\gamma}[n_{\gamma}(r)] = \gamma^{2} E_{1}[n(r)], \quad F_{\gamma}[n_{\gamma}(r)] = \gamma^{2} F_{1}[n(r)], \quad T_{\gamma}[n_{\gamma}(r)] = \gamma^{2} T_{1}[n(r)], \quad W_{\gamma}[n_{\gamma}(r)] = \gamma W_{1}[n(r)], \quad (25)$$

with the 1-body potential scaled as  $V^{\gamma}(r) = \gamma^2 V^1(\gamma r)$ .

Coming to the ingredients used in the ISI method the scaling becomes

$$W_0[n_{\gamma}(r)] = \gamma W_0[n(r)], \quad W'_0[n_{\gamma}(r)] = W'_0[n(r)], \quad W_{\infty}[n_{\gamma}(r)] = \gamma W_{\infty}[n(r)], \quad W'_{\infty}[n_{\gamma}(r)] = \gamma^{3/2} W'_{\infty}[n(r)], \quad (26)$$

where the auxiliary relationship  $W_{\alpha\gamma}[n_{\gamma}(r)] = \gamma W_{\alpha}[n(r)]$  is handy when taking the limits  $\alpha \to 0$  and  $\alpha \to \infty$ . In order to respect these conditions, an interaction strength interpolation formula

$$W_{\lambda}^{ISI}([n]) = F(\lambda, W_0[n], W_0'[n], W_{\infty}[n], W_{\infty}'[n])$$
(27)

must be such that

$$F(\lambda, \lambda W_0, W'_0, \lambda W_\infty, \lambda^{3/2} W'_\infty) = \lambda F(1, W_0, W'_0, W_\infty, W'_\infty)$$
(28)

or equivalenty

$$F(\lambda, W_0, W'_0, W_{\infty}, W'_{\infty}) = \lambda F(1, \frac{W_0}{\lambda}, W'_0, \frac{W_{\infty}}{\lambda}, \frac{W'_{\infty}}{\lambda^{3/2}})$$
(29)

for all accessible values of its arguments and any positive  $\lambda$ . Therefore the interaction energy at the physical strength ( $\lambda = 1$ ) can be used to define the scaled interaction strength at every scaling factor.

When moving to the interaction-energy density one finds that

$$n_{\gamma}^{(2)}(r,r',[n_{\gamma}]) = \gamma^6 n_1^{(2)}(\gamma r,\gamma r',[n]) \implies w_{\gamma}(r,[n_{\gamma}]) = \gamma^4 w_1(\gamma r,[n])$$
(30)

hence

$$w_0(r, [n_{\gamma}]) = \gamma^4 w_0(\gamma r, [n]), \qquad w'_0(r, [n_{\gamma}]) = \gamma^3 w'_0(\gamma r, [n]), \tag{31}$$

$$w_{\infty}(r, [n_{\gamma}]) = \gamma^{4} w_{\infty}(\gamma r, [n]), \qquad w'_{\infty}(r, [n_{\gamma}]) = \gamma^{4\frac{1}{2}} w'_{\infty}(\gamma r, [n]).$$
(32)

In order to respect these conditions, a local interaction strength interpolation formula

$$w_{\lambda}^{LIISA}(r,[n]) = f(\lambda, w_0(r,[n]), w_0'(r,[n]), w_{\infty}(r,[n]), w_{\infty}'(r,[n]), n(r))$$
(33)

must be such that

$$f(\lambda, \lambda^4 w_0, \lambda^3 w'_0, \lambda^4 w_\infty, \lambda^{4\frac{1}{2}} w'_\infty) = \lambda^4 f(1, w_0, w'_0, w_\infty, w'_\infty),$$
(34)

or

$$f(\lambda, w_0, w'_0, w_\infty, w'_\infty) = \lambda^4 f(1, \frac{w_0}{\lambda^4}, \frac{w'_0}{\lambda^3}, \frac{w_\infty}{\lambda^4}, \frac{w'_\infty}{\lambda^{4\frac{1}{2}}}),$$
(35)

for all values of its arguments and any positive  $\lambda$ .

It may be convenient in some cases, like in the homogeneous electron gas—that contains an infinite number of particles—to define the local quantities in a per-particle basis; though it may result somewhat artificial as the energy density is not really particle-based. However since everything is in the end a function of the density why not...

Let's define then  $w_{\lambda}(r, [n]) = n(r)\overline{w}_{\lambda}(r, [n])$  with  $\overline{w}_{\lambda}(r, [n])$  the interaction energy per particle associated to point r.

The resulting scaling relation is the same as for the integrated quantities but defined locally on the scale coordinate:

$$w_{\gamma}(r,[n_{\gamma}]) = \gamma^4 w_1(\gamma r,[n]) \implies \overline{w}_{\gamma}(r,[n_{\gamma}]) = \gamma \overline{w}_1(\gamma r,[n]), \tag{36}$$

hence

$$\overline{w}_0(r,[n_\gamma]) = \gamma \overline{w}_0(\gamma r,[n]), \qquad \overline{w}'_0(r,[n_\gamma]) = \overline{w}'_0(\gamma r,[n]), \qquad (37)$$

$$\overline{w}_{\infty}(r,[n_{\gamma}]) = \gamma \overline{w}_{\infty}(\gamma r,[n]), \qquad \overline{w}_{\infty}'(r,[n_{\gamma}]) = \gamma^{3/2} \overline{w}_{\infty}'(\gamma r,[n]), \tag{38}$$

and the associated local interaction strength interpolation formula, where an explicit dependence on the density has been added,

$$\overline{w}_{\lambda}^{LIISA}(r,[n]) = \overline{f}(\lambda, \overline{w}_0(r,[n]), \overline{w}_0'(r,[n]), \overline{w}_{\infty}(r,[n]), \overline{w}_{\infty}'(r,[n]))$$
(39)

must satisfy

$$\overline{f}(\lambda,\lambda\overline{w}_0,\overline{w}'_0,\lambda\overline{w}_\infty,\lambda^{3/2}\overline{w}'_\infty,\lambda^3n) = \lambda\overline{f}(1,\overline{w}_0,\overline{w}'_0,\overline{w}_\infty,\overline{w}'_\infty,n)$$
(40)

$$\overline{f}(\lambda, \overline{w}_0, \overline{w}'_0, \overline{w}_\infty, \overline{w}'_\infty, n) = \lambda \overline{f}(1, \frac{\overline{w}_0}{\lambda}, \overline{w}'_0, \frac{\overline{w}_\infty}{\lambda}, \frac{\overline{w}'_\infty}{\lambda^{3/2}}, \frac{n}{\lambda^3})$$
(41)

for all accessible values of its arguments and any positive  $\lambda$ .

### from interaction strength to correlation energy and return

let us remind the definition of the correlation energy

$$E_c[n] = \int_0^1 d\lambda \left( W_\lambda[n] - W_0[n] \right) \tag{42}$$

and the basic scaling relationship

$$W_{\lambda}[n_{\lambda}] = \lambda w_{1}[n] \implies W_{\lambda\alpha}[n_{\lambda}] = \lambda W_{\alpha}[n] \implies \begin{cases} W_{0}[n_{\lambda}] = \lambda W_{0}[n] \\ W_{\infty}[n_{\lambda}] = \lambda W_{\infty}[n] \end{cases}$$
(43)

then we can manipulate the above definition as

$$E_c[n_{\gamma}] = \int_0^1 d\lambda \left( W_{\lambda}[n_{\gamma}] - W_0[n_{\gamma}] \right) = \int_0^1 d\lambda \gamma \left( W_{\lambda/\gamma}[n] - W_0[n] \right) = \gamma^2 \int_0^{1/\gamma} d\lambda \left( W_{\lambda}[n] - W_0[n] \right).$$
(44)

Hence

$$\frac{d}{d\gamma} \left[ \frac{E_c[n_{\gamma}]}{\gamma^2} \right] = \frac{d}{d\gamma} \int_0^{1/\gamma} d\lambda \left( W_{\lambda}[n] - W_0[n] \right) = \left( W_{1/\gamma}[n] - W_0[n] \right) \frac{d}{d\gamma} \left( \frac{1}{\gamma} \right) = -\frac{1}{\gamma^2} \left( W_{1/\gamma}[n] - W_0[n] \right)$$
(45)

and finally

$$W_{\lambda}[n] = W_0[n] - \gamma^2 \frac{d}{d\gamma} \left[ \frac{E_c[n_{\gamma}]}{\gamma^2} \right], \quad \gamma = 1/\lambda \quad \Longrightarrow \quad W_{\lambda}[n] = W_0[n] + \frac{d}{d\lambda} \left[ \lambda^2 E_c[n_{1/\lambda}] \right], \tag{46}$$

and similarly for the per-particle quatities

$$\overline{w}_{\lambda}(r,[n]) = \overline{w}_{0}(r,[n]) - \gamma^{2} \frac{d}{d\gamma} \left[ \frac{\overline{\varepsilon}_{c}(r/\gamma,[n_{\gamma}])}{\gamma^{2}} \right], \gamma = 1/\lambda \quad \Longrightarrow \quad \overline{w}_{\lambda}(r,[n]) = \overline{w}_{0}(r,[n]) + \frac{d}{d\lambda} \left[ \lambda^{2} \overline{\varepsilon}_{c}(\lambda r,[n_{1/\lambda}]) \right],$$

$$\tag{47}$$

and the energy densities

$$w_{\lambda}(r,[n]) = w_{0}(r,[n]) - \gamma^{2} \frac{d}{d\gamma} \left[ \frac{\varepsilon_{c}(r/\gamma,[n_{\gamma}])}{\gamma^{5}} \right], \gamma = 1/\lambda \implies w_{\lambda}(r,[n]) = w_{0}(r,[n]) + \frac{d}{d\lambda} \left[ \lambda^{5} \varepsilon_{c}(\lambda r,[n_{1/\lambda}]) \right].$$

$$(48)$$

Therefore knowledge of the interaction energy as a function of the coupling constant for any given density allows to compute the correlation energy and, conversely, knowledge of the correlation energy for all scaled densities allows to compute the interaction energy as a function of the coupling constant.

## homogeneous electron gas: a case study

Let us see what all this bring us in the homegeneous electron gas case.

There is only one parameter defining the system, its uniform density or, conventionally, its Wigner-Seitz radius:  $n = \frac{3}{4\pi r_s^3}$ . The correlation energy per particle is a function of  $r_s$  whose functional dependence can be considered (numerically) known and have the known limiting behaviors:

$$\bar{\varepsilon}_c(r_s) = A \ln r_s + C + r_s(A_1 \ln r_s + C_1) + \dots, \quad r_s \sim 0,$$
(49)

$$\overline{\varepsilon}_{c}(r_{s}) = \frac{f_{0}}{r_{s}} + \frac{f_{1}}{r_{s}^{3/2}} + \frac{f_{2}}{r_{s}^{2}} + \dots, \qquad r_{s} \to \infty.$$
(50)

We can then calculate the interaction energy per particle

$$\overline{w}_{\lambda}(r_s) = \overline{w}_0(r_s) + \frac{d}{d\lambda} \left[ \lambda^2 \overline{\varepsilon}_c(\lambda r_s) \right] = \overline{w}_0(r_s) + \frac{1}{r_s} \frac{d}{dx} \left[ x^2 \overline{\varepsilon}_c(x) \right]_{x=\lambda r_s} = \lambda \left[ \overline{w}_0(x) + \frac{1}{x} \frac{d}{dx} \left( x^2 \overline{\varepsilon}_c(x) \right) \right]_{x=\lambda r_s},$$
(51)

or if you wish

$$\overline{w}_{\lambda}(r_s) = \lambda \overline{w}_1(\lambda r_s), \qquad \overline{w}_1(r_s) = \overline{w}_0(r_s) + \frac{1}{r_s} \frac{d}{dr_s} \left( r_s^2 \overline{\varepsilon}_c(r_s) \right) = \frac{f_x}{r_s} + \frac{1}{r_s} \frac{d}{dr_s} \left( r_s^2 \overline{\varepsilon}_c(r_s) \right), \tag{52}$$

that corresponds to the following conditions:

$$\overline{w}_0 = \frac{f_x}{r_s}, \quad \overline{w}'_0 = -\infty, \quad \overline{w}_\infty = \frac{f_x + f_0}{r_s}, \quad \overline{w}'_\infty = \frac{1}{2} \frac{f_1}{r_s^{3/2}}, \quad n = \frac{3}{4\pi r_s^3}$$
 (53)

which describe a one-dimesional line in a 5-dimesional parameter space describing the interaction energy per particle and could be used to constraint the LIISA interaction energy density interpolating function.

## other "solvable" models and the way to go

Other systems that one could study to extract information to define/constrain/train LIISA:

Helium-like atoms: 2 electrons that can be solved by full CI leading to a 2 dimensional slice of the energy density, parameterized by the nuclear charge and the radial distance.

Other spherical atoms that can be solved by full CI. Be to mention one and its isoelectronic series.

 $H_2$ -like molecular dissociation: 2 electrons that can be solved by full CI leading to a 5-dimensional exploration of the energy density parameterized by  $Z_1$ ,  $Z_2$ , (allowing the two nuclei to have different charges), R (the atoms' separation), z (the coordinate along the line connecting the nuclei),  $\rho$  (the radial cilindrical coordinate).

Other diatomic molecules with more electrons ( $Be_2$  to mention one) that would give access to different regions of the parameter space and/or sample the same regions thus providing a measure of the spread of the interaction energy density values corresponding to given parameters.

The challenge is how to visualize the collected information and see how strong is the variability of the interaction energy density in given regions of the parameter-space? Is it possible/accurate to express the energy density as a function of the coefficients of its weak- and strong-coupling limits? Does the energy density of all systems collapse on the same energy-density surface  $f^{LIISA}(\lambda, w_0, w'_0, w_\infty, w'_\infty)$  when parameterized by these values? how to incorporate deviation/additional knowledge in the process? adding an explicit dependence on n(r) and its detivatives? or space derivatives of the 'energy-density ingredients'? what else?

#### what about spin polarized systems?

To be understood at alater time ...

#### more about the interaction energy density

The total interaction energy operator is

$$\hat{W} = \frac{e^2}{2} \sum_{\substack{i,j \ i\neq j}} \frac{1}{|r_i - r_j|} \quad \text{or} \quad \hat{W} = \frac{e^2}{2} \int dx dy \frac{\phi^{\dagger}(x)\phi^{\dagger}(y)\phi(y)\phi(x)}{|x - y|}$$
(54)

in first and second quantization respectively.

The interaction energy density operator can therefore be defined as

$$\hat{w}(r) = \frac{e^2}{8\pi} \sum_{\substack{i,j\\i\neq j}} \nabla \frac{1}{|r-r_i|} \nabla \frac{1}{|r-r_j|} \quad \text{or} \quad \hat{w}(r) = \frac{e^2}{8\pi} \int dx dy \nabla \frac{\phi^{\dagger}(x)\phi^{\dagger}(y)}{|r-x|} \nabla \frac{\phi(y)\phi(x)}{|r-y|} \quad (55)$$

respectively.

The  $\lambda$ -dependent interaction energy density is therefore the expectation value of this operator on the GS wavefunction  $\Psi_{GS}^{\lambda}$  (or the density matrix  $\Gamma^{\lambda}$ ) corresponding to a given value of  $\lambda$ .

$$w_{\lambda}(r,[n]) = \langle \Psi_{GS}^{\lambda} | \hat{w}(r) | | \Psi_{GS}^{\lambda} \rangle = Tr \Gamma_{\lambda}[n] \hat{w}(r)$$
(56)

and the coupling constant could be considered position dependent and the functonal generalized to

$$F_{[\lambda]}[n] = \min_{\Psi \to n} \langle \Psi | \ \hat{T} + \int \lambda(r) \hat{w}(r) dr \ |\Psi\rangle = T_{[\lambda]}[n] + \int \lambda(r) w_{[\lambda]}(r, [n]) dr$$
(57)

The  $F_{[\lambda]}$  functionals are variational w.r.t. all (neutral) density variations, in particular all those generated by an arbitrary coupling constant variation,  $\lambda(r) \longrightarrow \lambda(r) + \delta\lambda(r)$ , hence:

$$\frac{\delta F_{[\lambda]}}{\delta\lambda(r)} = w_{[\lambda]}(r, [n]), \quad \frac{\delta T_{[\lambda]}}{\delta\lambda(r)} + \int \lambda(r'') \frac{\delta}{\delta\lambda(r)} w_{[\lambda]}(r'', [n]) \, dr' = 0, \quad \frac{\delta^2 T_{[\lambda]}}{\delta\lambda(r)\delta\lambda(r')} + \int \lambda(r'') \frac{\delta^2 w_{[\lambda]}(r'', [n])}{\delta\lambda(r)\delta\lambda(r')} \, dr'' > 0$$
(58)

where the last inequality has to be understood in a matrix sense and stems from the fact that each  $F_{[\lambda]}$  is a minimum w.r.t to density variations induced by any  $\delta\lambda$ . Taking a further variation of the above second equality one obtains

$$\frac{\delta^2 T_{[\lambda]}}{\delta\lambda(r)\delta\lambda(r')} + \int \lambda(r'') \frac{\delta^2 w_{[\lambda]}(r'', [n])}{\delta\lambda(r)\delta\lambda(r')} dr'' + \frac{\delta}{\delta\lambda(r)} w_{[\lambda]}(r', [n]) = 0$$
(59)

from where one can deduce that the last term must be a symmetric function of r and r' because the other two terms obviously are. Moreover comparing with the third inequality in the previous line one gets that it must be negative definite:

$$\delta w_{[\lambda]}(r, r', [n]) = \frac{\delta}{\delta\lambda(r)} w_{[\lambda]}(r', [n]) < 0$$
(60)

to be understood as a "matrix" inequality. In particular all diagonal elements are negative definite. This however is not enough to show that the derivative of  $w_{\lambda}(r, [n])$  with respect to a uniform scaling is negative definite.