

3. Total energy as functional of electron density

3.1 Expectation values of one- and two-particle operators

We remember the separation of a Hamiltonian into one-particle and two-particle operators in Eq. (2.12). It can be shown that the expectation value of any one-particle operator can be expressed in terms of one-particle density matrix, that of two-particle operator – in terms of two-particle matrix etc. We consider an arbitrary single-particle operator

$$\hat{F} = \sum_{i=1}^N \hat{f}(x_i) , \quad (3.1)$$

then its expectation value in a many-body state Ψ is

$$\begin{aligned} \langle \hat{F} \rangle &= \int dx_1 \dots dx_N \Psi^*(x_1 \dots x_N) \sum_{i=1}^N \hat{f}(x_i) \Psi(x_1 \dots x_N) = \\ &= \int dx \sum_{i=1}^N \hat{f}(x) \left[\int dx_2 \dots dx_N \Psi^*(y, x_2 \dots x_N) \Psi(x, x_2 \dots x_N) \right]_{y=x} . \end{aligned}$$

In doing so, we used the fact that simultaneous interchange of any two arguments in *both* Ψ^* and Ψ does not change their product,

$$\Psi^*(x_1 \dots x_i \dots x_N) \Psi(x_1 \dots x_i \dots x_N) = \Psi^*(x_i \dots x_1 \dots, x_N) \Psi(x_i \dots x_1 \dots x_N) ,$$

and the integration parameter y different from x was introduced in Ψ^* in order to ensure that the operator \hat{f} acts on Ψ only, not on Ψ^* . For a simple multiplication (e.g., \hat{f} being an external potential) this is not important so that one can simplify in the last formula $[\dots]_{y=x} \Rightarrow \int dx_2 \dots dx_N \Psi^*(x, x_2 \dots x_N) \Psi(x, x_2 \dots x_N)$, but if, e.g., $\hat{f} = \nabla^2$, then it is essential to keep first arguments in Ψ^* and Ψ formally different and set $y = x$ after the integration. With the definition of the density matrix (2.20),

$$\langle \hat{F} \rangle = \int [\hat{f}(x) \gamma(x; y)]_{y=x} dx , \quad (3.2)$$

or, considering both \hat{f} and γ as operators in the x -space,

$$\langle \hat{F} \rangle = \text{tr}(\hat{f} \gamma) , \quad (3.3)$$

For an operator \hat{f} depending only on the coordinates of particles (like external electrostatic field, or kinetic energy) the summation over spin components can be done in Eq. (3.2), resulting in

$$\langle \hat{F} \rangle = \int d\mathbf{r} [\hat{f}(\mathbf{r}) \gamma(\mathbf{r}; \mathbf{r}')]_{\mathbf{r}'=\mathbf{r}} . \quad (3.4)$$

If the spin degrees of freedom matter for the one-particle operator in question, then its expectation values can be expressed via spin-dependent single-particle density matrices. The vector spin operator $\hat{\sigma} = \sum_{\alpha} \mathbf{e}_{\alpha} \hat{\sigma}_{\alpha}$ is defined via cartesian unit vectors \mathbf{e}_{α} and Pauli matrices

$$\hat{\sigma}_z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \hat{\sigma}_x = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y = \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad (3.5)$$

then the vector spin density will be

$$\hat{\mathbf{S}}(\mathbf{r}) = \sum_{i=1}^N \hat{\sigma}_i \delta(\mathbf{r} - \mathbf{r}_i), \quad (3.6)$$

and the spin magnetization density

$$\mathbf{m}(\mathbf{r}) = 2 \langle \hat{\mathbf{S}}(\mathbf{r}) \rangle = 2 \sum_{ss'} \hat{\sigma}_{s's} \rho_{ss'}(\mathbf{r}) = 2 \text{tr}_s [\hat{\sigma} \gamma(\mathbf{r})] \quad (3.7)$$

with

$$\rho_{ss'}(\mathbf{r}) = \begin{pmatrix} \rho^{++}(\mathbf{r}) & \rho^{+-}(\mathbf{r}) \\ \rho^{-+}(\mathbf{r}) & \rho^{--}(\mathbf{r}) \end{pmatrix},$$

then

$$\mathbf{m}(\mathbf{r}) = \begin{cases} 2 \text{Re} \rho^{-+}(\mathbf{r}) \\ 2 \text{Im} \rho^{-+}(\mathbf{r}) \\ \rho^{++}(\mathbf{r}) - \rho^{--}(\mathbf{r}) \end{cases}. \quad (3.8)$$

Similarly, for any two-particle operator $\hat{V} = \frac{1}{2} \sum_{i \neq j} \hat{v}(x_i, x_j)$

$$\begin{aligned} \langle \hat{V} \rangle &= \frac{1}{2} \sum_{i \neq j} \int dx_1 \dots dx_N \Psi^*(x_1 \dots x_N) \hat{v}(x_i, x_j) \Psi(x_1 \dots x_N) = \\ &= \frac{1}{2} \sum_{i \neq j} \int dx dy \int \Psi^*(x, y, x_3 \dots x_N) \hat{v}(x, y) \Psi(x, y, x_3 \dots x_N) dx_3 \dots dx_N = \\ &\text{(using the same argument as above, interchanging } x_i \leftrightarrow x, x_j \leftrightarrow y \text{ in both } \Psi^* \text{ and } \Psi) \\ &= \int dx dy [\hat{v}(x, y) \gamma_2(x, y; x', y')]_{\substack{x'=x \\ y'=y}}. \end{aligned} \quad (3.9)$$

Again, we introduced x' independent from x and y' independent from y in order to prevent that operator $\hat{v}(x, y)$ acts on the arguments in Ψ^* . However, if $\hat{v}(x, y)$ is simple multiplication (as is the case with Coulombic two-particle interaction), this is not necessary, so one can write down using Eq. (2.41)

$$\langle \hat{V} \rangle = \frac{1}{2} \int dx dy v(x, y) \rho_2(x, y). \quad (3.10)$$

Therefore the expectation value of any operator in a certain state of a many-electron system can be obtained through the knowledge of two functions, the single-particle density matrix $\gamma(x, y)$ defined in Eq. (2.20) and the pair density $\rho_2(x, y)$ defined in Eq. (2.41).

3.2 Hohenberg–Kohn theorem

Of course the last statement applies to the total energy as the expectation value of the Hamilton operator in a particular state. However, if we consider specifically the *ground state*, the total energy must be extremal, that allows to formulate a more strong condition, as was done by Pierre Hohenberg and Walter Kohn in 1964⁸:

In the ground state, the total energy is a functional of the electron density $\rho(\mathbf{r})$.

That means actually that not only one doesn't need to know density matrix and the pair density to determine the ground-state total energy, but the dependence of the latter on spin variables is not relevant as well. We'll prove this *ad absurdum*, following the original derivation of Hohenberg and Kohn. Underway, we'll distinguish between what is sometimes referred to as the first Hohenberg–Kohn theorem and the second one.

We start by specifying once again the many-electron Hamiltonian,

$$\mathcal{H}[u] = -\underbrace{\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2}_{\equiv \hat{T}} + \underbrace{\sum_{i=1}^N u(x_i)}_{\equiv \hat{U}} + \underbrace{\frac{1}{2} \sum_{i \neq j}^N v(x_i, v_j)}_{\equiv \hat{V}} .$$

$u(x_i)$ is an external potential, and in the following we assume we are free to vary it. Each external potential defines a corresponding ground-state wavefunction via solution of the Schrödinger equation. Such wavefunctions are of course different for u_1 and u_2 , if $u_1(\mathbf{r}) \neq u_2(\mathbf{r}) + \text{const.}$. What about the particle density? It results from the integration over $N-1$ variables in the wavefunction. It will turn out that still, there is no way to get $\rho[u_1]$ the same as $\rho[u_2]$ if the potentials differ by more than a constant. But first we assume that this is possible. Let Ψ_1 be the ground-state wavefunction corresponding to the external potential u_1 , then the corresponding total energy is:

$$E_1 = \langle \Psi_1 | \mathcal{H}[u_1] | \Psi_1 \rangle = \langle \Psi_1 | \hat{T} + \hat{V} | \Psi_1 \rangle + \int u_1(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} .$$

This must be lower than the expectation value obtained with *any* other wavefunction Ψ_2 :

$$\begin{aligned} E_1 &< \langle \Psi_2 | \mathcal{H}[u_1] | \Psi_2 \rangle \\ E_1 &< \langle \Psi_2 | \mathcal{H}[u_2] - u_2 + u_1 | \Psi_2 \rangle \\ E_1 &< \underbrace{\langle \Psi_2 | \mathcal{H}[u_2] | \Psi_2 \rangle}_{E_2} + \int d\mathbf{r} [u_1(\mathbf{r}) - u_2(\mathbf{r})] \underbrace{N \int \Psi_2^*(\mathbf{r}_2 \dots \mathbf{r}_N) \Psi_2(\mathbf{r}_2 \dots \mathbf{r}_N) d\mathbf{r}_2 \dots d\mathbf{r}_N}_{=\rho(\mathbf{r})} . \end{aligned}$$

On the other side, the ground-state energy E_2 calculated with its “true” wavefunction Ψ_2 must be lower than the expectation value of $\mathcal{H}[u_2]$ calculated with any other wavefunction, including Ψ_1 :

$$\begin{aligned} E_2 &< \langle \Psi_1 | \mathcal{H}[u_2] | \Psi_1 \rangle \\ E_2 &< \langle \Psi_1 | \mathcal{H}[u_1] - u_1 + u_2 | \Psi_1 \rangle \\ E_2 &< \underbrace{\langle \Psi_1 | \mathcal{H}[u_1] | \Psi_1 \rangle}_{E_1} + \int d\mathbf{r} [u_2(\mathbf{r}) - u_1(\mathbf{r})] \underbrace{N \int \Psi_1^*(\mathbf{r}_2 \dots \mathbf{r}_N) \Psi_1(\mathbf{r}_2 \dots \mathbf{r}_N) d\mathbf{r}_2 \dots d\mathbf{r}_N}_{=\rho(\mathbf{r})} . \end{aligned}$$

⁸*Inhomogeneous Electron Gas*, Phys. Rev. **136**, B864 (1964)

Summing up two inequalities, we arrive at $E_1 + E_2 < E_2 + E_1$, that is a contradiction. The origin of this contradiction is that we assumed $\rho(\mathbf{r})$ to be the same for two wavefunctions generated by two different potentials u_1 and u_2 . Hence this assumption was wrong, and the external potential *uniquely* determines the density. Since $\rho[u_1] \neq \rho[u_2]$ for $u_1 \neq u_2 + \text{const}$, for any given $\rho(\mathbf{r})$ there is at most one potential $u(\mathbf{r})$ for which $\rho(\mathbf{r})$ is the ground-state density.

At this point, one sometimes singles out as the first Hohenberg–Kohn theorem:

For isolated many-electron system, its ground-state one-electron density $\rho(\mathbf{r})$ determines uniquely the external potential $u(\mathbf{r})$

and as the second Hohenberg–Kohn theorem:

The exact ground state energy $E = E[\Psi_0]$ of many-electron system with external potential $u(\mathbf{r})$ is a functional of the associated ground-state electron density $\rho_0(\mathbf{r})$.

This second statement follows from the fact that since $u(\mathbf{r})$ uniquely fixes \mathcal{H} and hence the many-particle ground state, the latter must be a unique functional of $\rho(\mathbf{r})$:

$$E[\rho_0(\mathbf{r})] = T[\Psi_0] + V[\Psi_0] + \int d\mathbf{r} u(\mathbf{r}) \rho(\mathbf{r}). \quad (3.11)$$

As a brief discussion, it is important to emphasize the following:

- this is simply an existence theorem, which tells absolutely nothing about the actual dependence of the kinetic part $T[\Psi_0[u[\rho(\mathbf{r})]]]$ and the electron-electron interaction part $V[\Psi_0[u[\rho(\mathbf{r})]]]$ in the total energy on particle density. This is a serious challenge for practical applications.
- there is a problem of u -representability, i.e. a question of whether an arbitrary function $\rho(\mathbf{r})$ can be mapped onto corresponding $u(\mathbf{r})$. There has been a history of works aimed at more strict mathematical formulation.

3.3 Kohn–Sham equation

There are two essential problems of applying Eq. (3.11) to practical calculations: the concretization of $T[\rho]$ and $V[\rho]$. The Thomas–Fermi theory provides approximations for both, but they are not accurate enough, particularly in what regards the kinetic energy part. Walter Kohn and Lu Sham in 1965⁹ proposed a trick allowing to represent the kinetic energy better.

In a many-electron system without interaction (V switched off), the ground-state wavefunction (when non-degenerate) is a single Slater determinant. Then the kinetic energy can be easily evaluated:

$$\begin{aligned} \mathcal{H}_0 &= \hat{T}_0 + u(\mathbf{r}); & \Psi_0 &= \frac{1}{\sqrt{N!}} \det \|\varphi_i(x_k)\|; \\ T_0[\Psi_0] &= \langle \Psi_0 | \hat{T} | \Psi_0 \rangle = -\frac{\hbar^2}{2m} \sum_{i=1}^N \langle \varphi_i | \nabla_i^2 | \varphi_i \rangle. \end{aligned} \quad (3.12)$$

⁹Phys. Rev. **140**, A1133 (1965)

The particle density is $\rho(\mathbf{r}) = \sum_{is} \varphi_i^*(x) \varphi_i(x)$, as in the HF formalism, Eq. (2.19). With the interaction actually present, the representation for the density can still be applied, understanding that $\varphi_i(x)$ are not true one-particle wavefunctions anymore, but just any support functions, or pseudofunctions, of our convenience to represent the density. This is fully general. Further on, we approximate the kinetic energy of a true system by \hat{T}_0 constructed from $\{\varphi_i\}$ according to Eq. (3.12). This introduces an error, which is further on attributed to the yet undefined part, which describes electron-electron interaction. The functions $\varphi_i(x)$ are searched for using variational approach (instead of searching for $\rho(x)$ directly, as in the Thomas-Fermi formalism). Once $\{\varphi_i\}$ are found, we can immediately reconstruct the density. Specifically, the total energy from Eq. (3.11)

$$E_{tot} = T[\rho] + \underbrace{\frac{e^2}{2} \int \frac{\rho(x)\rho(x')}{|\mathbf{r}-\mathbf{r}'|} dx dx'}_{\text{Coulomb interaction, including self-interaction}} + \underbrace{E_{XC}[\rho]}_{\text{corrections: exchange + correlation, so good we can}} + e \int u(x)\rho(x) dx \quad (3.13)$$

$\underbrace{\hspace{15em}}_{V[\rho]}$

will be substituted by

$$E_{tot} = \underbrace{T_0[\rho]}_{\text{kinetic energy of non-interacting system of } N \text{ particles with the same density}} + \frac{e^2}{2} \int \frac{\rho(x)\rho(x')}{|\mathbf{r}-\mathbf{r}'|} dx dx' + \underbrace{E'_{XC}[\rho]}_{E_{XC}+T[\rho]-T_0[\rho]} + e \int u(x)\rho(x) dx . \quad (3.14)$$

We apply the variational approach, searching for those pseudofunctions $\varphi_i(x)$ which would minimize the total energy. From Eq. (3.12)

$$\frac{\delta T_0}{\delta \varphi_\alpha^*(x)} = -\frac{\hbar^2}{2m} \nabla^2 \varphi_\alpha(x) ; \quad \frac{\delta \rho(x')}{\delta \varphi_\alpha^*(x)} = \varphi_\alpha(x) \delta(x-x') ;$$

$$\frac{\delta}{\delta \varphi_\alpha^*(x)} \left[\frac{1}{2} \int \frac{\rho(x)\rho(x')}{|\mathbf{r}-\mathbf{r}'|} dx dx' \right] = \left[\int \frac{\rho(x)}{|\mathbf{r}-\mathbf{r}'|} dx \right] \varphi_\alpha(x) ;$$

hence

$$\frac{\delta}{\delta \varphi_\alpha^*(x)} \left\{ T_0[\rho] + \frac{e^2}{2} \int \frac{\rho(x)\rho(x')}{|\mathbf{r}-\mathbf{r}'|} dx dx' + E'_{XC}[\rho] + e \int u(x)\rho(x) dx - \varepsilon_\alpha \left[\int \rho(x) d\mathbf{r} - N \right] \right\} = 0 . \quad (3.15)$$

where the Lagrange multipliers ε_α , as before, take care of maintaining the normalization of the density in the course of variation. The variation of (yet unknown) XC-functional

in φ_α^* can be reformulated via its variation in ρ :

$$\frac{\delta E'_{\text{XC}}}{\delta \varphi_\alpha^*(x)} = \int dx' \frac{\delta E'_{\text{XC}}}{\delta \rho(x')} \underbrace{\frac{\delta \rho(x')}{\delta \varphi_\alpha^*(x)}}_{\delta(x-x') \varphi_\alpha(x)} = \underbrace{\frac{\delta E'_{\text{XC}}}{\delta \rho(x)}}_{\text{XC-potential, } V_{\text{XC}}(x)} \varphi_\alpha(x).$$

Eq. (3.13) then reduces to

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + e^2 \int dx' \frac{\rho(x')}{|\mathbf{r} - \mathbf{r}'|} + u(x) + V_{\text{XC}}(x) - \varepsilon_\alpha \right] \varphi_\alpha(x) = 0. \quad (3.16)$$

This is the system of equations resembling that of the HF method after introducing the Slater averaging for exchange – the equations are linear in φ_α , which mix via the contribution of all of them to the total density. The Slater averaged exchange potential V_{X} can be considered as an approximation to a more general V_{XC} . V_{XC} is a simple function of \mathbf{r} (and spin), but it depends on the distribution of density in the whole space.

However, the present derivation is more general; it does not impose any particular restrictions on the wave function (we assumed for it a single-determinant form only in the absence of electron-electron interaction, in order to construct T_0).

- This rearrangement puts everything yet unknown into $V_{\text{XC}}(x)$; the rest is explicitly defined.
- The equations give φ_α and then total density, but provide absolutely no information about the ground-state wavefunction (not even about the density matrix).
- Everything applies to the ground state only – that is nevertheless quite important, because problems like equilibrium structure, magnetization, phonons, etc. fall into this category.
- This approach essentially fixes the problems of the Thomas-Fermi method related to poor description of the kinetic energy.

The closed form for the ground-state total energy in the Kohn–Sham approach can be obtained from Eq. (3.14), using T_0 as defined by Eq. (3.12):

$$T_0[\rho] = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m} \right) \int \varphi_i^*(x) \nabla^2 \varphi_i(x) dx$$

from Eq. (3.16)

$$-\frac{\hbar^2}{2m} \nabla^2 \varphi_\alpha(x) = \varepsilon_\alpha \varphi_\alpha(x) - \left[u(x) + V_{\text{XC}}(x) + e^2 \int \frac{\rho(x')}{|\mathbf{r} - \mathbf{r}'|} dx' \right] \varphi_\alpha(x),$$

that results in

$$\begin{aligned} E_{\text{tot}} &= \sum_{i=1}^N \int \varphi_i^*(x) \varepsilon_i \varphi_i(x) dx - \sum_{i=1}^N \int \varphi_i^*(x) V_{\text{XC}}(x) \varphi_i(x) dx - \\ &- e^2 \sum_{i=1}^N \int dx \varphi_i^*(x) \varphi_i(x) \int \frac{\rho(x')}{|\mathbf{r} - \mathbf{r}'|} dx' + \frac{e^2}{2} \int \frac{\rho(x)\rho(x')}{|\mathbf{r} - \mathbf{r}'|} dx dx' + E'_{\text{XC}}[\rho] = \\ &= \sum_{i=1}^N \varepsilon_i - \frac{e^2}{2} \int \frac{\rho(x)\rho(x')}{|\mathbf{r} - \mathbf{r}'|} dx dx' - \int V_{\text{XC}}(x) \rho(x) dx + E'_{\text{XC}}[\rho]. \end{aligned} \quad (3.17)$$

$\{\varepsilon_i\}$ is a set of N lowest eigenvalues of the Kohn–Sham equations, similarly to the *aufbau principle* in the HF method.

3.4 Relation between exchange-correlation energy and electron pair correlation function

We already discussed earlier that the exchange and correlation are essentially due to a Coulomb interaction of each electron with electron density *missing* in its environment, so no wonder that E_{XC} can be directly related to the pair density $\rho_2(x, y)$ defined by Eq. (2.41). However, one must consider that E'_{XC} incorporates as well the difference between the true kinetic energy T and that of non-interacting electron gas of the same density, T_0 . We model this situation by an adiabatic approximation: scale the electron-electron interaction in the Hamiltonian with λ , $0 \leq \lambda \leq 1$, and assure that the density $\rho(x)$ remains the same for all values of λ by adding a corresponding λ -dependent external potential u_λ :

$$\mathcal{H} = \mathcal{H}_0 + \lambda \mathcal{W} = \sum_i \hat{h}_i^{(\lambda)} + \lambda \sum_{ij} \hat{w}_{ij}. \quad (3.18)$$

For all λ along the part $0 \rightarrow 1$, there is a ground-state function Ψ_λ and total energy E_λ . Taking into account

$$\frac{\partial}{\partial \lambda} \langle \Psi_\lambda | \Psi_\lambda \rangle = 0 = \left\langle \frac{\partial \Psi_\lambda}{\partial \lambda} | \Psi_\lambda \right\rangle + \left\langle \Psi_\lambda | \frac{\partial \Psi_\lambda}{\partial \lambda} \right\rangle,$$

we get:

$$\begin{aligned} \frac{\partial}{\partial \lambda} E_\lambda &= \left\langle \frac{\partial \Psi_\lambda}{\partial \lambda} | \mathcal{H} | \Psi_\lambda \right\rangle + \left\langle \Psi_\lambda | \frac{\partial \mathcal{H}}{\partial \lambda} | \Psi_\lambda \right\rangle + \left\langle \Psi_\lambda | \mathcal{H} | \frac{\partial \Psi_\lambda}{\partial \lambda} \right\rangle = \\ &= E_\lambda \left[\left\langle \frac{\partial \Psi_\lambda}{\partial \lambda} | \Psi_\lambda \right\rangle + \left\langle \Psi_\lambda | \frac{\partial \Psi_\lambda}{\partial \lambda} \right\rangle \right] + \left\langle \Psi_\lambda | \frac{\partial \mathcal{H}}{\partial \lambda} | \Psi_\lambda \right\rangle = \\ &= \left\langle \Psi_\lambda | \mathcal{W} | \Psi_\lambda \right\rangle. \end{aligned} \quad (3.19)$$

This is the Hellmann–Feynman theorem. Then the total energy can be recovered as

$$E = E_0 + \int_0^1 d\lambda \langle \Psi_\lambda | \mathcal{W} | \Psi_\lambda \rangle, \quad (3.20)$$

Assuming that we switch on the interaction adiabatically, i.e. $d\lambda/dt \rightarrow 0$ and the system is everywhere in the ground state, we specify the Hamiltonian as

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_0 + \sum_i u_\lambda(x_i) + \frac{e^2}{2} \sum_{i \neq j} \frac{\lambda}{|\mathbf{r}_i - \mathbf{r}_j|}; \\ \frac{d\mathcal{H}}{d\lambda} &= \sum_i \frac{du_\lambda(x_i)}{d\lambda} + \frac{e^2}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \end{aligned}$$

To calculate its expectation value, we use Eq. (3.2) and (3.10). Since both operators here are simply numbers, one does not need to care about $y \rightarrow x$ in (3.2) and writes simply in terms of single and pair density:

$$\langle \Psi_\lambda | \sum_i \frac{du_\lambda(x_i)}{d\lambda} | \Psi_\lambda \rangle = \int \frac{du_\lambda(x)}{d\lambda} \rho(x) dx ; \quad (3.21)$$

$$\langle \Psi_\lambda | \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \Psi_\lambda \rangle = \int \frac{\rho(x, x')}{|\mathbf{r} - \mathbf{r}'|} dx dx' , \quad (3.22)$$

We express the pair density in terms of pair correlation function g (2.42), which gets the dependence on λ (the single-particle density is the same for all λ , but the correlation function and hence the pair density certainly not):

$$\rho(x, x') = g_\lambda(x, x') \rho(x) \rho(x') . \quad (3.23)$$

$$\frac{dE_\lambda}{d\lambda} = \int \rho(x) \frac{\partial u_\lambda(x)}{\partial \lambda} dx + \frac{e^2}{2} \int \frac{\rho(x) \rho(x')}{|\mathbf{r} - \mathbf{r}'|} g_\lambda(x, x') dx dx' .$$

Then

$$\begin{aligned} E - E_0 &= \int_0^1 \frac{dE_\lambda}{d\lambda} d\lambda = \int \rho(x) [u_{\lambda=1}(x) - u_{\lambda=0}(x)] dx + \\ &+ \frac{e^2}{2} \int \frac{\rho(x) \rho(x')}{|\mathbf{r} - \mathbf{r}'|} dx dx' \int_0^1 g_\lambda(x, x') d\lambda . \end{aligned} \quad (3.24)$$

Without interaction,

$$E_0 = T_0[\rho] + \int \rho(x) u_{\lambda=0}(x) dx ,$$

with full interaction (3.14)

$$E = T_0[\rho] + \frac{e^2}{2} \int \frac{\rho(x) \rho(x')}{|\mathbf{r} - \mathbf{r}'|} dx dx' + \int \rho(x) u_{\lambda=1}(x) dx + E'_{\text{XC}}[\rho] ;$$

hence

$$E - E_0 = \frac{e^2}{2} \int \frac{\rho(x) \rho(x')}{|\mathbf{r} - \mathbf{r}'|} dx dx' + \int \rho(x) [u_{\lambda=1}(x) - u_{\lambda=0}(x)] dx + E'_{\text{XC}}[\rho] ,$$

and comparing with (3.24) one gets:

$$E'_{\text{XC}}[\rho] = \frac{e^2}{2} \int \frac{\rho(x) \rho(x')}{|\mathbf{r} - \mathbf{r}'|} [\tilde{g}(x, x') - 1] dx dx' . \quad (3.25)$$

with

$$\tilde{g}(x, x') = \int_0^1 g_\lambda(x, x') d\lambda . \quad (3.26)$$

Hence the *exact* exchange-correlation energy is fully determined by the shape of the exchange-correlation hole (but, for the full range of interaction strengths).

3.5 E_{XC} for homogeneous electron liquid

A large amount of useful information about general properties of $E_{\text{XC}}[\rho]$ has been obtained in the course of simulating a simple benchmark system, homogeneous electron liquid. This is a system of interacting electrons with homogeneous density, compensated by equally homogeneous background positive charge.

We begin with some general considerations, in order to incorporate the effect of spin polarization in the following treatment. We start from the exchange energy and then generalize the results over the correlation energy. Introducing explicitly spin variables, we get

$$E_{\text{X}} = -\frac{e^2}{2} \iint \frac{\rho_{\text{X}}^{(+)}(\mathbf{r}, \mathbf{r}') \rho^{(+)}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' - \frac{e^2}{2} \iint \frac{\rho_{\text{X}}^{(-)}(\mathbf{r}, \mathbf{r}') \rho^{(-)}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \quad (3.27)$$

since exchange interaction does not “mix” two spin components. Therefore

$$E_{\text{X}}[\rho^{(+)}, \rho^{(-)}] = E_{\text{X}}[\rho^{(+)}] + E_{\text{X}}[\rho^{(-)}]. \quad (3.28)$$

Further on, we introduce exchange energy *density* $\epsilon_{\text{X}}(\mathbf{r})$ that satisfies

$$E_{\text{X}} = \int d\mathbf{r} \epsilon_{\text{X}}(\mathbf{r}) \rho(\mathbf{r}) \quad (3.29)$$

without loss of generality.¹⁰ Comparing it with Eq. (3.27)

$$\rho(\mathbf{r}) \epsilon_{\text{X}}(\mathbf{r}) = -\frac{e^2}{2} \int \frac{\rho_{\text{X}}^{(+)}(\mathbf{r}, \mathbf{r}') \rho^{(+)}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' - \frac{e^2}{2} \int \frac{\rho_{\text{X}}^{(-)}(\mathbf{r}, \mathbf{r}') \rho^{(-)}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (3.30)$$

For uniform electron gas of constant density $\rho^{(+)}$ and $\rho^{(-)}$, we may perform the integration in Eq. (3.30) in analogy with (2.38). We emphasize that it doesn't matter how the total density is split into $\rho^{(+)}$ and $\rho^{(-)}$; the integration limit in \mathbf{k} -space is fixed by the ρ value in each spin channel separately. Therefore we use, instead of (2.37) where it was assumed $\rho^{(+)} = \rho/2$, explicitly

$$\rho_{\text{X}}^{(+)}(\mathbf{r}, \mathbf{r}') = 9\rho^{(+)} \left[\frac{j_1(k_{\text{F}}|\mathbf{r} - \mathbf{r}'|)}{k_{\text{F}}|\mathbf{r} - \mathbf{r}'|} \right]^2;$$

instead of (2.35) we have

$$\frac{k_{\text{F}}^3}{6\pi^2} = \rho^{(+)}; \quad k_{\text{F}} = (6\pi^2 \rho^{(+)})^{1/3}.$$

The integration over $\mathbf{r}'' = \mathbf{r}' - \mathbf{r}$, with fixed \mathbf{r} , yields:

$$\begin{aligned} \int 9\rho^{(+)} \left[\frac{j_1(k_{\text{F}}|\mathbf{r} - \mathbf{r}'|)}{k_{\text{F}}|\mathbf{r} - \mathbf{r}'|} \right]^2 \frac{\rho^{(+)}}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' &= 9 [\rho^{(+)}]^2 \cdot 4\pi \int_0^\infty r''^2 dr'' \left[\frac{j_1(k_{\text{F}}r'')}{k_{\text{F}}r''} \right]^2 \frac{1}{r''} = \\ &= \frac{36\pi}{(6\pi^2)^{2/3}} [\rho^{(+)}]^{4/3} \underbrace{\int_0^\infty \frac{(\sin x - x \cos x)^2}{x^5} dx}_{1/4} = 3 \left(\frac{3}{4\pi} \right)^{1/3} [\rho^{(+)}]^{4/3}. \end{aligned} \quad (3.31)$$

¹⁰this is *not* yet local density approximation as long as $\epsilon_{\text{X}}(\mathbf{r})$ depends on the density in *all* space, not just at \mathbf{r} .

Further on, we introduce spin polarization $\zeta(\mathbf{r})$

$$\zeta = \frac{\rho^{(+)} - \rho^{(-)}}{\rho} \quad \text{with} \quad \rho = \rho^{(+)} + \rho^{(-)}, \quad (3.32)$$

whence

$$\rho^{(+)} = \frac{\rho}{2}(1 + \zeta), \quad \rho^{(-)} = \frac{\rho}{2}(1 - \zeta);, \quad (3.33)$$

and exchange energy density, now dependent on spin polarization, becomes:

$$\epsilon_X(\mathbf{r}, \zeta) = -\frac{3e^2}{2} \left(\frac{3}{4\pi}\right)^{1/3} \frac{\rho^{1/3}}{2^{4/3}} \left[(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3}\right]. \quad (3.34)$$

In the following, we'll use instead of ρ the density parameter r_s , that is the radius of a sphere including unit charge,

$$\frac{4\pi}{3} r_s^3 \rho = 1 \quad \rightarrow \quad r_s = \left(\frac{3}{4\pi\rho}\right)^{1/3}. \quad (3.35)$$

Note that r_s is \mathbf{r} -dependent for inhomogeneous density distribution. With this definition,

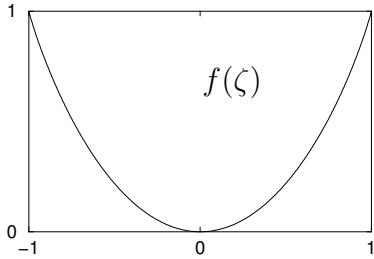
$$\epsilon_X(\mathbf{r}, \zeta) = -\frac{3e^2}{4\pi} \left(\frac{9\pi}{4}\right)^{1/3} \frac{(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3}}{2r_s}. \quad (3.36)$$

In what regards the dependence on the spin polarization, the exchange energy density can be looked at as an interpolation between limiting values of ‘‘paramagnetic’’ ($\zeta=0$) and ‘‘ferromagnetic’’ ($\zeta=1$) cases,

$$\epsilon_X(\mathbf{r}, 0) = -\frac{3e^2}{4\pi} \left(\frac{9\pi}{4}\right)^{1/3} \cdot \frac{2}{2r_s}, \quad \epsilon_X(\mathbf{r}, 1) = -\frac{3e^2}{4\pi} \left(\frac{9\pi}{4}\right)^{1/3} \cdot \frac{2^{4/3}}{2r_s},$$

so that

$$\epsilon_X(\mathbf{r}, \zeta) = \epsilon_X(\mathbf{r}, 0) + [\epsilon_X(\mathbf{r}, 1) - \epsilon_X(\mathbf{r}, 0)] f(\zeta), \quad (3.37)$$



with

$$f(\zeta) = \frac{(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3} - 2}{2^{4/3} - 2} \quad (3.38)$$

known as the von Barth – Hedin interpolation function (see plot).

Von Barth and Hedin calculated¹¹ the correlation energy of spin-polarized electron liquid in the lowest order in the random phase approximation for different values of ζ and r_s . It follows that the same interpolation function is accurate enough for correlation energy density, so that one can use:

$$\epsilon_{XC}(\mathbf{r}, \zeta) = \epsilon_{XC}(\mathbf{r}, 0) + [\epsilon_{XC}(\mathbf{r}, 1) - \epsilon_{XC}(\mathbf{r}, 0)] f(\zeta). \quad (3.39)$$

¹¹U. von Barth and L. Hedin, *A local exchange-correlation potential for the spin polarized case: I*, J. Phys. C: **5**, 1629 (1972).

The exact results analysis of $\epsilon_{\text{XC}}(r_s)$ are not so far known even for the simplest model case of free *electron liquid*, or jellium – a homogeneous distribution of interacting electrons at the background of uniformly smeared compensating positive charge. The analytic results have been obtained (up to certain accuracy) only for limiting cases of low and high densities. The high-density limit ($r_s \rightarrow 0$) in the paramagnetic case is given by

$$\begin{aligned} \epsilon_{\text{XC}}(r_s, 0) = & -\frac{3}{4\pi} \left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{r_s} && \text{already described by Eq. (3.36)} \\ & + \frac{1 - \ln 2}{\pi^2} \ln r_s && \text{W. Macke,} \\ & && \text{Z. Naturforsch. } \mathbf{5a}, 192 \text{ (1950)} \\ & \left. \begin{aligned} & + B \\ & + C r_s \ln r_s \\ & + D r_s \end{aligned} \right\} && \text{Carr + Maradudin,} \\ & && \text{Phys. Rev. } \mathbf{133}, \text{A371 (1964)} \\ & + \dots && \end{aligned}$$

The solution for the ferromagnetic case is known in the random phase approximation:¹²

$$\epsilon_{\text{XC}}^{\text{RPA}}(\rho, 1) = \frac{1}{2} \epsilon_{\text{XC}}^{\text{RPA}}(2^4 \rho, 0). \quad (3.40)$$

This scaling is consistent with Eq. (3.36) for the exchange energy density.

The low-density limit is essentially that of electron crystallization, i.e. their localization near well separated (and ordered) positions in space. The possibility of such behaviour at sufficiently low densities was first recognized by E. Wigner.¹³ Wigner compared different crystal lattices by their contributions to the total energy – essentially, Madelung terms evaluated by Ewald summation. The results obtained for several lattice types are:

-1.79186 r_s^{-1} Ry	(body centered cubic)
-1.79172	(face centered cubic)
-1.79168	(hexagonal close-packed)
-1.760...	(simple cubic)

As is seen, the bcc lattice seems to be the most probable candidate for the Wigner crystallization of jellium, but it is not strictly proven, and at least fcc and hcp lattices become competitive. The excitations from the “crystallized” state are electron lattice vibrations, or “phonons”. With zero-point energy of such “phonons” taken into account, the perturbation expansion in the low-density limit is in powers of $r_s^{-1/2}$ and yields (in

¹²L. Hedin, Phys. Rev. **139**, A796 (1965)

¹³E. Wigner, Trans. Faraday Soc. **34**, 678 (1938)

the paramagnetic case) for the energy in Ry per electron – see, e.g., Carr (1961):¹⁴

$$\begin{aligned}
 E = & -\frac{1.792}{r_s} && \text{Madelung energy of Wigner crystal} \\
 & + \frac{2.66}{r_s^{3/2}} && \text{zero-point energy} \\
 & \left. + \frac{b}{r_s^2} \right\} && \text{perturbations to} \\
 + O\left(\frac{1}{r_s^{5/2}}\right) & && \text{oscillator functions; } b < 1 \\
 + \text{terms } \sim \exp(-r_s^{1/2}) & &&
 \end{aligned}$$

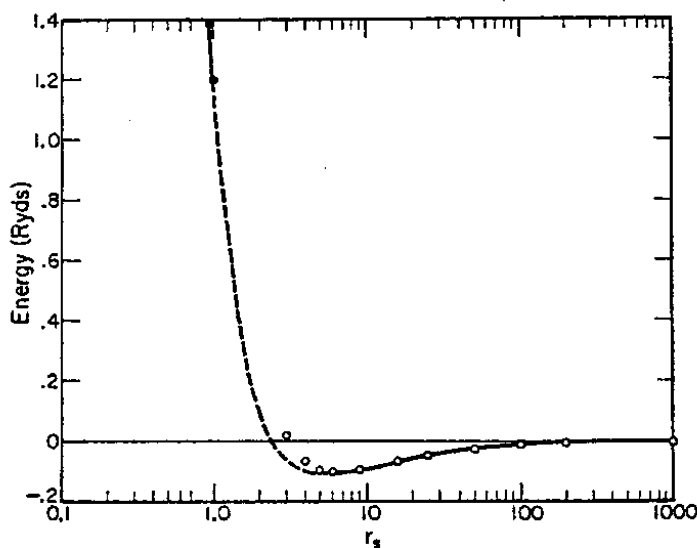


Fig. 1 of Carr (1961). Energy of the electron gas plotted against r_s . The open circles are points given by the above formula with anharmonic terms neglected. The filled circles were calculated from the Gell-Mann and Brueckner equation [Phys. Rev. **106**, 364 (1957)]. In constructing the dashed line connecting the two end regions, consideration was given to the fact that it must fall below the sum of Fermi plus exchange energy for plane waves. The open circle points below $r_s=6$ have lower accuracy, since for these points the exponential terms are appreciable.

The above figure shows the estimations of exchange-correlation energy of homogeneous electron liquid obtained by perturbation expansion in two limiting cases. The solid curve is a free interpolation connecting the data in small r_s and large r_s regions. The region of “relevant” r_s values is 2 – 7 a.u., where none of limiting approximations works well. A number of calculations has been done by Hedin and Lundqvist, von Barth and Hedin, Gunnarsson and Lundqvist¹⁵ to bridge the region of intermediate r_s for both paramagnetic and ferromagnetic cases. For example, the parametrization of the correlation energy density by Hedin and Lundqvist¹⁶ ($\zeta=0$ case), adopted also by von Barth and Hedin for the $\zeta=1$ case, uses the function

$$F(z) = (1 + z^3) \ln \left(1 + \frac{1}{z} \right) + \frac{z}{2} - z^2 - \frac{1}{3}$$

¹⁴W. J. Carr, Jr., *Energy, Specific Heat, and Magnetic Properties of the Low-Density Electron Gas*, Phys. Rev. **122**, 1437 (1961).

¹⁵O. Gunnarsson and B. I. Lundqvist, *Exchange and correlation in atoms, molecules, and solids by the spin-density-functional formalism*, Phys. Rev. B **13**, 4274 (1976).

¹⁶L. Hedin and B. I. Lundqvist, *Explicit local exchange-correlation potentials*, J. Phys. C **4**, 2064 (1971).

and

$$\epsilon(r_s, 0) = -C^{\text{PM}} F\left(\frac{r_s}{r^{\text{PM}}}\right), \quad \epsilon(r_s, 1) = -C^{\text{FM}} F\left(\frac{r_s}{r^{\text{FM}}}\right),$$

with parameter values (r_s in a.u., energy in Ry):

$$C^{\text{PM}} = 0.0504; \quad C^{\text{FM}} = 0.0254; \quad r^{\text{PM}} = 30; \quad r^{\text{FM}} = 75.$$

This is consistent (within 1%) with the scaling relation (3.40) for the random phase approximation:

$$C^{\text{FM}} = \frac{1}{2} C^{\text{PM}}; \quad r^{\text{FM}} = 2^{4/3} r^{\text{PM}}.$$

For more accurate parametrizations in the intermediate range of r_s , it was extremely important that (ultimately exact) results of Monte Carlo simulation became available due to Ceperley and Alder.¹⁷ Their scheme was a search for “optimized” many-body wavefunction and its corresponding energy in a diffusion process, starting from a trial wavefunction and an arbitrary reference energy. The trial function was a product of two-body correlation factors (that remove singularities in the local energy as electrons approach each other) times a Slater determinant, constructed either from plane-wave states (for Fermi liquid), or from bcc-centered Gaussians (for the Wigner crystal). Paramagnetic or ferromagnetic case was fixed in advance.

With the Hamiltonian of usual form,

$$\mathcal{H} = \frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 - \frac{e^2}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|},$$

the parameter space \mathcal{R} includes $3N$ spatial coordinates of the system of N electrons. A random walk in $d\mathcal{R}^{3N}$ at time t is given by $f(\mathcal{R}, t) \cdot d\mathcal{R}^{3N}$, f being the probability density. The value of f at $t=0$ is $|\Psi_{\text{T}}(\mathcal{R})|$, e.g., starting trial function. For large times,

$$f(\mathcal{R}, t \rightarrow \infty) = \Psi_{\text{T}}(\mathcal{R}) \varphi_0 \exp[-t(E_{\text{ref}} - E_0)],$$

with φ_0 as asymptotic (“true”) wavefunction and E_0 – “true” eigenvalue. The diffusion equation for $f(\mathcal{R}, t)$ is

$$\frac{\partial f}{\partial t} = \frac{\hbar^2}{2m} \left[\sum_{i=1}^N \nabla_i^2 f - \nabla_i \left(f \nabla_i \ln |\Psi_{\text{T}}|^2 \right) \right] - \underbrace{\left[\frac{\mathcal{H}\Psi_{\text{T}}}{\Psi_{\text{T}}} - E_{\text{ref}} \right]}_{\text{trial energy}} f$$

and implies:

- random diffusion;
- drift induced by the trial “quantum force” $\nabla \ln |\Psi_{\text{T}}|^2$
(since $\ln |\Psi_{\text{T}}|^2$ has the meaning of energy);
- branching with probability = (time step) $\times (E_{\text{trial}} - E_{\text{ref}})$.

¹⁷D. M. Ceperley and B. J. Alder, *Ground State of the Electron Gas by a Stochastic Method*, Phys. Rev. Lett. **45**, 566 (1980).

For $E_{\text{trial}} > E_{\text{ref}}$, the configuration is removed from the ensemble, for $E_{\text{trial}} < E_{\text{ref}}$ – duplicated in the ensemble.

The results of Ceperley and Alder are organized in a table of ground-state energies for several simulation objects (paramagnetic Fermi liquid, ferromagnetic Fermi liquid, Wigner crystal, and Bose liquid) over a range of r_s . These results can be also represented as the following “phase diagram”:

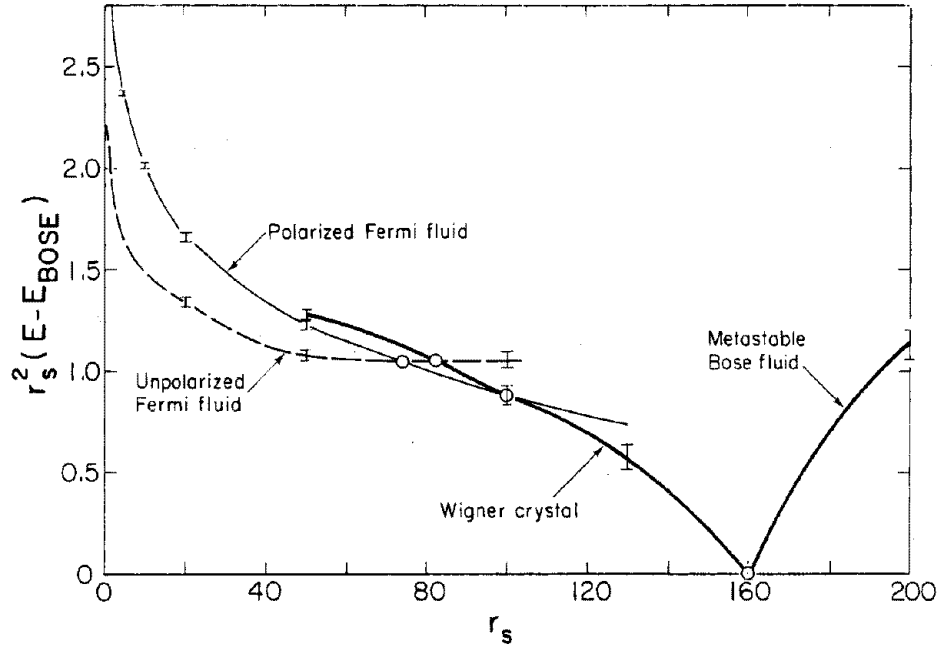


Fig. 2 of Ceperley and Alder. The energy of the four phases studied relative to that of the lowest boson state times r_s^2 in rydbergs vs r_s in Bohr radii. Below $r_s=160$ the Bose fluid is the most stable phase, while above, the Wigner crystal is most stable. The energies of the polarized and unpolarized Fermi fluid are seen to intersect at $r_s=75$. The polarized (Ferromagnetic) Fermi fluid is stable between $r_s=75$ and $r_s=100$, the Fermi Wigner crystal above $r_s=100$, and the normal paramagnetic Fermi fluid below $r_s=75$.

A number of analytical expressions interpolating the results by Ceperley and Alder has been proposed, which are now widely in use (Perdew and Zunger 1981 and others).

3.6 Local density approximation

The expression used for the exchange-correlation energy, in analogy with Eq. (3.29),

$$E_{\text{XC}} = \int d\mathbf{r} \epsilon_{\text{XC}}(\mathbf{r}) \rho(\mathbf{r}) ,$$

is quite general, as long as we assume ϵ_{XC} to be a function of \mathbf{r} , dependent on the whole distribution of density, i.e., $\epsilon_{\text{XC}}[\rho(\mathbf{r})]$. However, the benchmark studies we just discussed refer to the case of homogeneous density and are not, strictly speaking, applicable to varying $\rho(\mathbf{r})$. The local density approximation (LDA) represents an ill-justified but reasonable

generalization, that is expected to work at least for the case of slowly varying density:

$$E_{\text{XC}}^{\text{LDA}}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_{\text{XC}}(\rho(\mathbf{r}), \zeta(\mathbf{r})) . \quad (3.41)$$

We'll see that the accuracy of this approximation is better than could be *a priori* expected. The exchange-correlation potential $V_{\text{XC}}(\mathbf{r})$ as introduced in by Eq. (3.16) can be generalized for the spin-polarited case as follows:

$$\frac{\delta E_{\text{XC}}}{\delta \varphi_{\alpha}^*(x)} = \int \frac{\delta E_{\text{XC}}}{\delta \rho^{(+)}(x')} \underbrace{\frac{\delta \rho^{(+)}(x')}{\delta \varphi_{\alpha}^*(x)}}_{\delta(x'-x)\varphi_{\alpha}(x)} dx' = \frac{\delta E_{\text{XC}}}{\delta \rho^{(+)}} \varphi_{\alpha}(x)$$

is φ_{α} contributes to, say, spin (+), so that

$$V_{\text{XC}}^{(+)}(\mathbf{r}) = \frac{\partial}{\partial \rho^{(+)}(\mathbf{r})} \left\{ \rho(\mathbf{r}) \epsilon(\rho(\mathbf{r}), \zeta(\mathbf{r})) \right\} .$$

There is no more integration in spatial coordinates since

$$\frac{\partial}{\partial \rho(\mathbf{r})} \int \dots d\mathbf{r}' = \int \frac{\partial \dots}{\partial \rho(\mathbf{r})} \delta(\mathbf{r} - \mathbf{r}') d\mathbf{r}' .$$

The differentiation in spin-resolved components of density, taking into account relations (3.32), reduces to

$$\begin{aligned} \frac{\partial}{\partial \rho^{(+)}} &= \frac{\partial}{\partial \rho} \frac{\partial \rho}{\partial \rho^{(+)}} + \frac{\partial}{\partial \zeta} \frac{\partial \zeta}{\partial \rho^{(+)}} = \frac{\partial}{\partial \rho} + \frac{1 - \zeta}{\rho} \frac{\partial}{\partial \zeta} ; \\ \frac{\partial}{\partial \rho^{(-)}} &= \frac{\partial}{\partial \rho} - \frac{1 + \zeta}{\rho} \frac{\partial}{\partial \zeta} . \end{aligned}$$

Then

$$\begin{aligned} V_{\text{XC}}^{(\pm)}(\mathbf{r}) &= \epsilon_{\text{XC}}(\rho(\mathbf{r}), \zeta(\mathbf{r})) + \rho(\mathbf{r}) \frac{\partial \epsilon_{\text{XC}}(\rho(\mathbf{r}), \zeta(\mathbf{r}))}{\partial \rho} \pm [1 \mp \zeta(\mathbf{r})] \frac{\partial \epsilon_{\text{XC}}(\rho(\mathbf{r}), \zeta(\mathbf{r}))}{\partial \zeta} \\ &\equiv V_{\text{XC}}^{\text{LDA}(\pm)}(\rho(\mathbf{r}), \zeta(\mathbf{r})) . \end{aligned} \quad (3.42)$$

Since the energy won't change in case of simultaneous reversal of all spins, $\epsilon_{\text{XC}}(\rho(\mathbf{r}), \zeta(\mathbf{r})) = \epsilon_{\text{XC}}(\rho(\mathbf{r}), -\zeta(\mathbf{r}))$, and

$$\frac{\partial \epsilon_{\text{XC}}(\rho, -\zeta)}{\partial \zeta} = -\frac{\partial \epsilon_{\text{XC}}(\rho, \zeta)}{\partial \zeta} , \quad \text{hence} \quad V_{\text{XC}}^{(+)}(\rho, -\zeta) = V_{\text{XC}}^{(-)}(\rho, \zeta) .$$

Although seemingly poorly justified, the LDA works in practical calculations surprizingly well. The reason is that the XC energy is the integral over the XC hole of density times Coulomb interaction, see Eq. (3.25). The Coulomb interaction is spherically symmetric and leaves only spherically averaged, around \mathbf{r} , part of $\rho_{\text{XC}}(\mathbf{r}, \mathbf{r}')$ to contribute to E_{XC} .

The discussion to this effect can be found in the paper by Gunnarsson *et al.*¹⁸ and in the review by Jones and Gunnarsson¹⁹ and can be illustrated by the following figures, which show the cuts of the exact exchange hole in the Ne atom in comparison with its local density approximation. The actual shape of the exchange hole is drastically different from the approximated one (the true exchange hole in an atom has maximum at the nucleus whereas the averaged one is centered at the electron). However, the results of averaging over angles (with the center taken at the electron) are much closer for exact and LDA cases; moreover, only the radial integral of the angular-averaged function (times density and the Coulomb factor) actually affects the exchange energy.

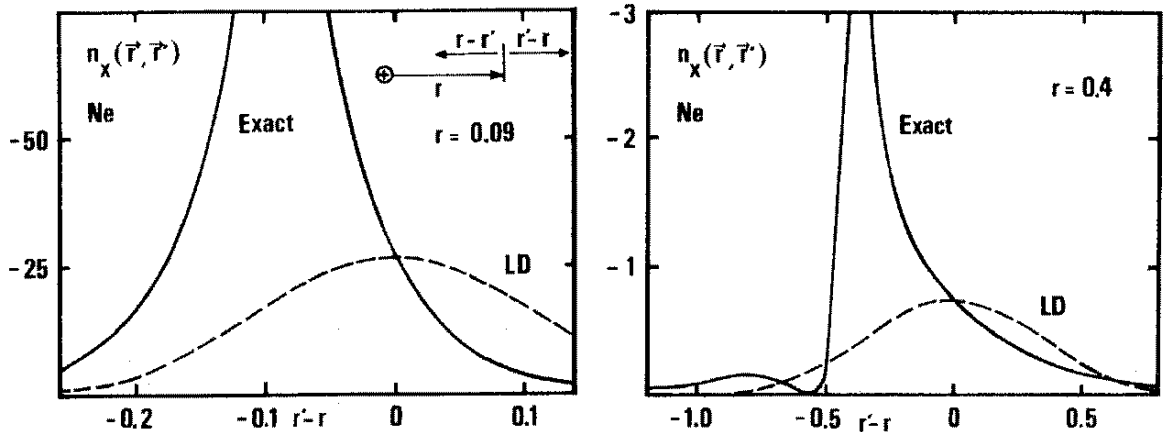


Fig. 5 of the Gunnarsson *et al.* (1979) paper. The exchange hole around an electron at r in the neon atom shown as a function of distance from the electron along a line connecting the electron and the nucleus. Full curves: the exact hole, dashed curves: the LDA result. Two panels correspond to the electron at two different distances from the nucleus, 0.09 and 0.4 a.u.

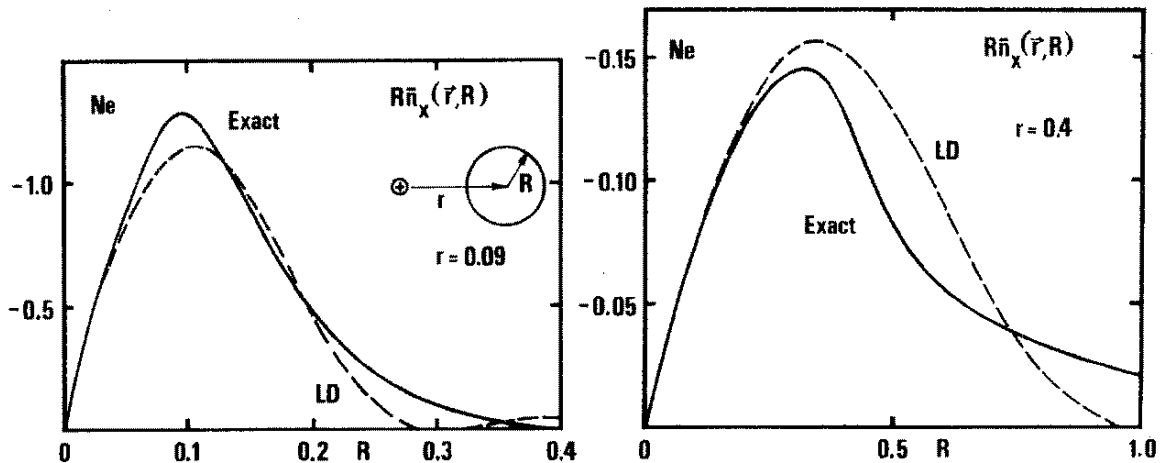


Fig. 7 of the Gunnarsson *et al.* (1979) paper. Spherical average of the neon exchange hole shown above.

¹⁸O. Gunnarsson, M. Jonson and B. I. Lundqvist, *Description of exchange and correlation effects in inhomogeneous electron systems*, Phys. Rev. B **20**, 3136 (1979).

¹⁹R. O. Jones and O. Gunnarsson, *The density functional formalism, its applications and prospects*, Rev. Mod. Phys. **61**, 689 (1989).

Qualitatively, the success of the LDA even for such unhomogeneous densities as that in atoms can be traced to the fact that an important sum rule is by construction implemented in the LDA: the exchange-correlation hole is integrated to -1 everywhere in space, i.e., for $E_{\text{XC}}[\rho]$ generally defined as

$$E_{\text{XC}}[\rho] = \frac{e^2}{2} \int \frac{\rho(\mathbf{r}) \rho_{\text{XC}}(\mathbf{r}, \mathbf{r}' - \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \quad (3.43)$$

$$\int \rho_{\text{XC}}(\mathbf{r}, \mathbf{r}' - \mathbf{r}) d\mathbf{r}' = -1 \quad \text{for all } \mathbf{r}. \quad (3.44)$$

If one separates exchange-correlation hole into exact exchange part (as would follow from the HF treatment) and the correlation part as the rest, the corresponding sum rules would be

$$\int \rho_{\text{X}}(\mathbf{r}, \mathbf{r}' - \mathbf{r}) d\mathbf{r}' = -1; \quad \int \rho_{\text{C}}(\mathbf{r}, \mathbf{r}' - \mathbf{r}) d\mathbf{r}' = 0.$$

The LDA substitutes

$$\frac{e^2}{2} \int \frac{\rho_{\text{XC}}(\mathbf{r}, \mathbf{r}' - \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \Rightarrow \epsilon_{\text{XC}}(\rho(\mathbf{r}))$$

where the XC-energy density is some function of $\rho(\mathbf{r})$ only. Because of this, density may appear only as a prefactor to the integral over \mathbf{r}' and not in the integral over \mathbf{r}' :

$$\rho_{\text{XC}}^{\text{LDA}}(\mathbf{r}, \mathbf{r}' - \mathbf{r}) = \rho(\mathbf{r}) [\tilde{g}(\mathbf{r}, \mathbf{r}') - 1],$$

where \tilde{g} is the correlation function integrated over interaction strength, see Eq. (3.26).

The performance of LDA in real systems with chemical bonding (solids, molecules) has been addressed in large number of publications. When discussing ground-state properties, one can note that the equilibrium volume is usually within $-5 - 0\%$ of the experiment, i.e. almost always underestimated, that reflects the fact that the LDA somehow overestimates the chemical bonding. Results for the bulk modulus, or generally on elastic constants, vary from very good to hardly satisfactory; actually calculated elastic properties are quite sensitive to a practical realization of DFT calculation (i.e., on the accuracy of representing a general-shape charge density). The same applies to the calculation of phonon frequencies. For cohesive energies, the following table gives some idea about the accuracy of LDA results. MJW (Moruzzi – Janak – Williams) and VW (Vosko – Wilk) are two different “flavours”, i.e. different parametrizations of the LDA energy density.

Cohesive energy (in eV) calculated using the LDA

	Li	Na	K	Be	Sr	Al
LDA-MJW	1.65	1.12	0.90	3.97	1.89	3.84
LDA-VW	1.74	1.21	0.96			
Exp.	1.66	1.26	0.94	3.33	1.70	3.34

Still, the error of LDA in reproducing ground-state properties is sometimes larger than acceptable; there are some known errors in the equation of state (wrong crystal structure in the ground state of Fe etc.)

3.7 Self-interaction correction

One of shortcomings of LDA is the presence of spurious self-interaction. It leads to noticeable errors in light atoms (especially hydrogen) and in systems with strongly localized states. Let us consider the hydrogen atom,

$$\rho^{(+)} = |\phi(\mathbf{r})|^2; \quad \rho^{(-)} = 0; \quad \zeta = 1.$$

The exact expression for the XC energy would be:

$$E_{\text{XC}} = -\frac{e^2}{2} \int \frac{|\phi(\mathbf{r})|^2 |\phi(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}',$$

that exactly cancels Hartree energy (there is no electron density to interact with). Comparing to the general expression (3.25), we see that this corresponds to vanishing correlation function, $\tilde{g}(\mathbf{r}; \mathbf{r}') = 0$. In LDA, the XC energy is constructed implying some non-zero correlation function. Explicitly for hydrogen atom, the electrostatic self-energy (e.g., Hartree term) of 8.5 eV is canceled by the XC energy of -8.1 eV to $\approx 95\%$.

A possible (not quite satisfactory) cure is to introduce explicit dependency on the index of one-particle functions (Kohn–Sham orbitals) into the functional to be optimized. This procedure is called *self-interaction correction* (SIC):

$$E^{\text{SIC}} = E^{\text{LDA}}[\rho(\mathbf{r}), \zeta(\mathbf{r})] - \sum_{i\sigma} \Theta_{i\sigma}, \quad (3.45)$$

$$\text{with } \Theta_{i\sigma} = \frac{e^2}{2} \int \frac{\rho_{i\sigma}(\mathbf{r}) \rho_{i\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E^{\text{LDA}}(\rho_{i\sigma}(\mathbf{r}), 1). \quad (3.46)$$

Each correction term $\Theta_{i\sigma}$ involves the contribution to the density from the Kohn–Sham orbital in question, which, if occupied, carries one electron and is hence fully spin-polarized:

$$\rho_{i\sigma}(\mathbf{r}) = \begin{cases} |\varphi_{i\sigma}(\mathbf{r})|^2, & \varphi_{i\sigma} \text{ occupied,} \\ 0, & \text{otherwise} \end{cases}$$

Similarly to the derivation of Kohn–Sham equations, Eq. (3.16), the variation of individual $\varphi_{i\sigma}$ yields:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + e^2 \int \frac{\rho(x')}{|\mathbf{r} - \mathbf{r}'|} dx + u(x) + V_{\text{XC},\alpha}^{\text{SIC}}(x) - \varepsilon_\alpha \right] \varphi_\alpha(x) = 0, \quad (3.47)$$

where $V_{\text{XC},\alpha}^{\text{SIC}}(x)$, now taking place of $V_{\text{XC}}(x)$, is:

$$V_{\text{XC},\alpha}^{\text{SIC}}(x) = V_{\text{XC}}[\rho, \zeta](x) - V_{\text{XC}}[\rho_\alpha, 1](x) - \int \frac{\rho_\alpha(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (3.48)$$

In a sense, some similarity to the HF treatment is thus recovered (since there is no spurious self-interaction in the HF), but $V_{\text{XC}}(x)$ may well include correlation effects beyond the exchange as well. The problems in the SIC scheme are the following:

- The Hamiltonian is formally different for different Kohn–Sham functions, that results

in non-orthogonality of the orbitals;

- The scheme is *not* invariant under a unitary transformation of the orbitals (i.e., different results may be obtained when using the basis of spherical harmonics or cubic harmonics).

Other useful extensions beyond the LDA can be sorted out into two groups. One group of approximations deals with certain assumptions about the shape of the XC hole, using, for instance, appropriate model functions. The other group of approximations proceeds with treating inhomogeneities in a systematic way – either by Taylor expansion, or Fourier expansion, of partially varying density. Let us consider several examples from both groups.

3.8 Averaged density approximation and Weighted density approximation

These two approximations have been proposed and discussed in the above cited paper by Gunnarsson – Jonson – Lundqvist (1979). The *Averaged density approximation* (ADA) uses, instead of density ρ at \mathbf{r} only, an average of density over some vicinity of \mathbf{r} . The XC-density is then represented by

$$\rho_{\text{XC}}^{\text{ADA}}(\mathbf{r}, \mathbf{r}' - \mathbf{r}') = \overline{\rho(\mathbf{r})} \int_0^1 [g(\mathbf{r} - \mathbf{r}', \lambda, \overline{\rho(\mathbf{r})}) - 1] d\lambda, \quad (3.49)$$

where g is some reasonable model for the pair correlation function. The averaging procedure for ρ is not uniquely predetermined, and the freedom existing in its choice can be exploited to satisfy certain important criteria, like the sum rule (3.44) and consistency with LDA results in the limit of constant density. Using such criteria, Gunnarsson *et al.* (1979) constructed the differential equation for the averaging function w that yields

$$\overline{\rho(\mathbf{r})} = \int w(\mathbf{r} - \mathbf{r}', \overline{\rho(\mathbf{r})}) \rho(\mathbf{r}') d\mathbf{r}',$$

and solved this equation numerically. This approximation has not been widely used so far.

The *Weighted density approximation* (WDA) uses another prescription for the XC-density,

$$\rho_{\text{XC}}^{\text{WDA}}(\mathbf{r}, \mathbf{r}' - \mathbf{r}') = \rho(\mathbf{r}') G(|\mathbf{r} - \mathbf{r}'|, \tilde{\rho}(\mathbf{r})) \quad (3.50)$$

that has the advantage of keeping a correct prefactor in the XC-density, compare Eqs. (3.25) and (3.43). $\tilde{\rho}(\mathbf{r})$ is again an in some way averaged density, and $G(r, \rho)$ is a model for the pair correlation function that doesn't have to be exact; one is free to choose a convenient analytical form which would guarantee the sum rule and correct asymptotics. A choice by Gunnarsson and Jones²⁰

$$G(r, \rho) = C(\rho) \left\{ 1 - \exp \left[-\frac{\lambda(\rho)}{|r|^5} \right] \right\}. \quad (3.51)$$

²⁰O. Gunnarsson and R. O. Jones, Phys. Scr. **21**, 394 (1980); R. O. Jones and O. Gunnarsson, *The density functional formalism, its applications and prospects*, Rev. Mod. Phys. **61**, 689 (1989).

Two conditions,

$$\rho \int G(|\mathbf{r}|, \rho) d\mathbf{r} = -1$$

and

$$\rho \frac{e^2}{2} \int \frac{G(|\mathbf{r}|, \rho)}{|\mathbf{r}|} d\mathbf{r} = \epsilon_{\text{XC}}(\rho),$$

allow to determine $C(\rho)$ and $\lambda(\rho)$. The asymptotic of (3.51) is such that several important limiting cases are described correctly. The WDA can be constructed to be exact in the following cases:

- (1) for homogeneous system;
- (2) for one-electron system, such as hydrogen atom (exact cancellation of the electron self-interaction);
- (3) for an atom, it provides correct asymptotic of the XC-energy far from nucleus,

$$\epsilon_{\text{XC}}(\mathbf{r}) = -\frac{e^2}{2r};$$

- (4) far outside the crystal surface, the correct asymptotic of image potential is recovered:

$$\epsilon_{\text{XC}}(z) = -\frac{e^2}{4z}.$$

For comparison, the LDA holds only for (1), for (2) the cancellation is only partial, and the criteria (3) and (4) are not satisfied.

Singh²¹ tested several flavours of WDA for ground-state properties of solids. According to present-day experience, the WDA provides considerable improvement over LDA in the description of ground-state properties for essentially all systems. A selection of some results by Singh is given in the following table.

Ground-state properties calculated within WDA by Singh (1993, 1998).
 a is lattice constant (in Å), B - bulk modulus (in GPa)

	C		GaAs		V		KNbO ₃	SrO
	a	B	a	B	a	B	a	a
LDA	3.53	483	5.62	85	2.93	215	3.96	5.06
WDA	3.57	404	5.74	62	3.00	145	4.02	5.16
Exp.	3.57	442	5.65	75	3.02	157	4.02	5.16

²¹David J. Singh, *Weighted-density-approximation ground-state studies of solids*, Phys. Rev. B **48**, 14099 (1993); I. I. Mazin and D. J. Singh, *Weighted Density Functionals for ferroelectric Materials*, <http://xxx...cond-mat/9801301>

3.9 Inhomogeneities of density: k -space analysis and gradient expansions

Another approach to inhomogeneities of particle density involves the Fourier transformation and analysis of terms dependent on wavevector (of charge fluctuations). Below, we follow the analysis of “inhomogeneous electron gas” in the original paper by Hohenberg and Kohn.

Consider the total energy functional as

$$E[\rho] = \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + \frac{e^2}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + G[\rho], \quad (3.52)$$

where $G[\rho]$ incorporates kinetic and exchange-correlation parts (the expression for the rest is exact). We assume that spatial deviations of density from its mean value are small,

$$\rho(\mathbf{r}) = \rho_0 + \tilde{\rho}(\mathbf{r}), \quad \text{with } \frac{\tilde{\rho}(\mathbf{r})}{\rho_0} \ll 1 \quad \text{everywhere.}$$

Moreover, the normalization (number of particles) remains constant, that leads to

$$\int \tilde{\rho}(\mathbf{r}) d\mathbf{r} = 0.$$

One can imagine the following formal expansion of $G[\rho]$ in $\tilde{\rho}$ as small parameter:

$$\begin{aligned} G[\rho] &= G[\rho_0] + \int I(\mathbf{r}) \tilde{\rho}(\mathbf{r}) d\mathbf{r} + \\ &+ \int K(\mathbf{r}, \mathbf{r}') \tilde{\rho}(\mathbf{r}) \tilde{\rho}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \\ &+ \int L(\mathbf{r}, \mathbf{r}', \mathbf{r}'') \tilde{\rho}(\mathbf{r}) \tilde{\rho}(\mathbf{r}') \tilde{\rho}(\mathbf{r}'') d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' + \dots \end{aligned} \quad (3.53)$$

The linear expansion coefficient must be zero, because the result cannot depend on the uniform shift $\mathbf{\Delta}$ of the coordinate system:

$$\int I(\mathbf{r}) \tilde{\rho}(\mathbf{r}) d\mathbf{r} = \int I(\mathbf{r}) \tilde{\rho}(\mathbf{r} - \mathbf{\Delta}) d\mathbf{r}, \quad \text{hence } \int [I(\mathbf{r}) - I(\mathbf{r} + \mathbf{\Delta})] \tilde{\rho}(\mathbf{r}) d\mathbf{r} = 0 \quad \text{for any } \mathbf{\Delta};$$

therefore $I(\mathbf{r}) = \text{const}$, and $\int I \tilde{\rho}(\mathbf{r}) d\mathbf{r} = 0$, due to normalization of $\tilde{\rho}(\mathbf{r})$.

Similarly, the 2nd-order kernel $K(\mathbf{r}, \mathbf{r}')$ can only depend on $|\mathbf{r} - \mathbf{r}'|$, because the result must be independent on the displacement of the $\tilde{\rho}(\mathbf{r})$ distribution, as well as on rotations about the $(\mathbf{r} - \mathbf{r}')$ line. We skip the following terms in the expansion (3.53) for the moment, so

$$G[\rho] = G[\rho_0] + \int K(|\mathbf{r} - \mathbf{r}'|) \tilde{\rho}(\mathbf{r}) \tilde{\rho}(\mathbf{r}') d\mathbf{r} d\mathbf{r}'. \quad (3.54)$$

We introduce the Fourier transformation of the quadratic kernel,

$$K(\mathbf{r} - \mathbf{r}') = \frac{1}{\Omega} \sum_{\mathbf{k}} K(k) e^{-i\mathbf{k}(\mathbf{r} - \mathbf{r}')} \quad (3.55)$$

and analyze the properties of $K(k)$. For this, we introduce a small parameter λ in the Fourier expansion of density:

$$\rho(\mathbf{r}) = \rho_0 + \frac{\lambda}{\Omega} \sum_{\mathbf{r}} b(\mathbf{k}) e^{-i\mathbf{k}\mathbf{r}}. \quad (3.56)$$

Hohenberg and Kohn argue that $K(k)$ can be related (comparing terms with the same powers of λ in the perturbation theory series for the interaction energy) to the electronic polarizability $\alpha(k)$, or to dielectric constant $\varepsilon(k)$ of the electronic liquid:

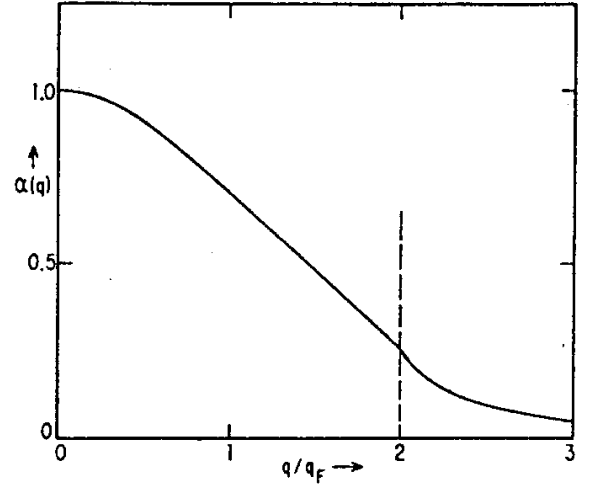
$$K(k) = \frac{2\pi}{k^2} \left[\frac{1}{\alpha(k)} - 1 \right] = \frac{2\pi}{k^2} \frac{1}{\varepsilon(k) - 1} \quad (3.57)$$

$$\text{with } \varepsilon(k) = \frac{E \text{ (primary field)}}{E - \underbrace{E \cdot \alpha}_{\text{induced field}}} = \frac{1}{1 - \alpha(k)}.$$

The polarizability $\alpha(k)$ has the following general properties:

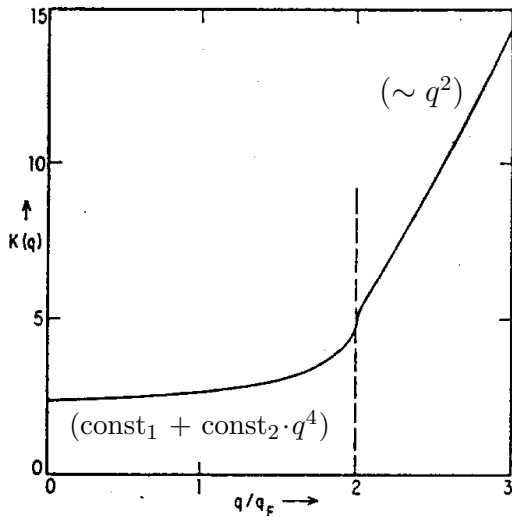
$$\begin{aligned} k \rightarrow 0 : & \quad a(k) = 1 + c_2 k^2 + c_4 k^4 + \dots \\ q \rightarrow 2k_F : & \quad \frac{d\alpha}{dk} \rightarrow -\infty; \\ q \rightarrow \infty : & \quad a(q) \sim \frac{1}{q^4}. \end{aligned}$$

Fig. 1 of Hohenberg and Kohn (1964). Electronic polarizability $\alpha(q)$, for electron density $= 4 \times 10^{22} \text{ cm}^{-3}$.



For free electron gas, $\varepsilon(k)$ is given by the Lindhard function, that leads for $K(k)$:

$$K(k) = \frac{4\pi}{k^2} \cdot \frac{k^2}{8k_F} \left[\frac{1}{2} + \frac{k_F}{2q} \left(1 - \frac{k^2}{4k_F^2} \right) \ln \left| \frac{k + 2k_F}{k - 2k_F} \right| \right]^{-1}. \quad (3.58)$$



The prefactor $4\pi/k^2$ is the Fourier transform of the Coulomb interaction, and the rest – Fourier transform of the correlation function. In order to discuss exchange-correlation hole separately, we concentrate in the following on the *exchange-correlation local field factor*

$$I_{XC}(k) = \frac{k^2}{4\pi} K_{XC}(k).$$

Fig. 2 of Hohenberg and Kohn (1964). Behavior of the kernel $K(q)$, for the same electron density.

Here, $K_{XC}(k)$ refers to the XC part of the kernel only, with the contribution due to kinetic energy of non-interacting particles subtracted.

For $I_{XC}(k)$, Monte Carlo results are available for several values of r_c , as well as different analytical approximations. Actually, any model concretizing the exchange-correlation energy density, be it LDA or different flavours of WDA, can be mapped onto a corresponding local-field XC factor. Examples have been given, e.g., by Mazin and Singh (1998).²²

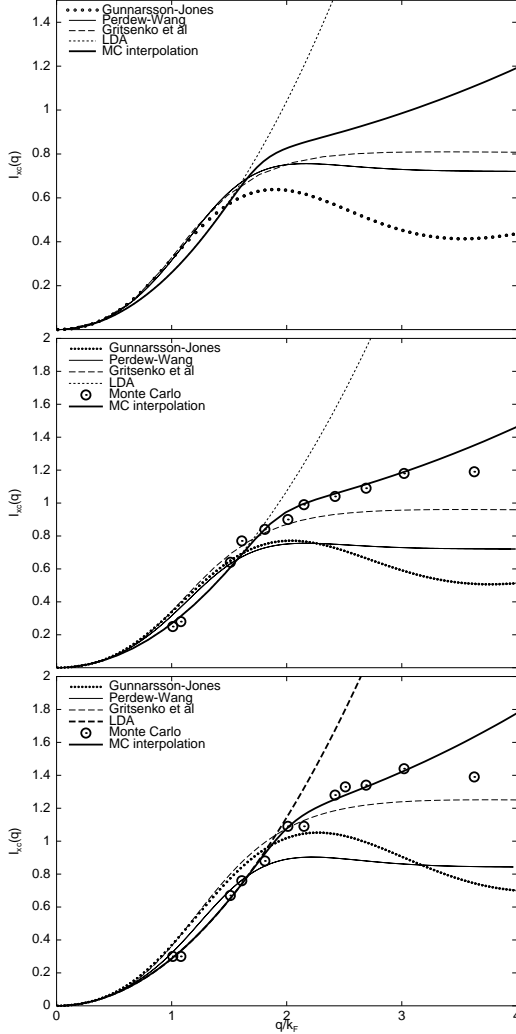


Fig. 1 of Mazin and Singh (1998). Exchange-correlation local field factor in the WDA by Gunnarsson and Jones 1980 (Phys. Scr. **21**, 394), Gritsenko *et al.* 1993 (Chem. Phys. Lett. **205**, 348), and derived from the homogeneous electron gas pair correlation function, Perdew and Wang 1993 (Phys. Rev. B **46**, 12947), as compared with the Monte Carlo results and the interpolating formula thereof, as given by Moroni, Ceperley and Senatore 1995 (Phys. Rev. Lett. **75**, 689). Densities, from top to bottom, correspond to $r_s=1, 2, 5$.

One can see that the LDA prescription for the local field factor proceeds as $K_{XC}(0)/(4\pi) \cdot k^2$, and it is a quite good approximation if fluctuations of density are of long wavelength, $k < 2k_F$. At $k = 2k_F$, the local-field factor, as the kernel $K(k)$ in general, experiences a kink, that gives rise to Friedel oscillations of electron density in the direct space. Beyond $2k_F$, $I_{XC}(k)$ increases $\sim k^2$ rather than tending to a constant; this is an indication that E_{XC} includes some kinetic-energy part.

A different method of taking into account inhomogeneities of density is via gradient expansions. One can construct the following expression for the energy density:

$$g[\rho] = g_0(\rho) + \sum_{i=1}^3 g_i(\rho) \nabla_i \rho + \sum_{ij}^3 [g_{ij}^{(1,1)}(\rho) \nabla_i \rho \nabla_j \rho + g_{ij}^{(2)} \nabla_i \nabla_j \rho] + \dots \quad (3.59)$$

If the density is scaled as

$$\rho(\mathbf{r}) = \rho' \left(\frac{\mathbf{r}}{r_0} \right),$$

²²I. I. Mazin and D. J. Singh, *Nonlocal density functionals and the linear response of the homogeneous electron gas*, Phys. Rev. B **57**, 6879 (1998)

the above series is an expansion in powers of (r_0^{-1}) . It does not strictly converge. However, we'll use it to sort out leading terms, including gradients of density. The validity of the gradient expansion requires

$$\frac{|\nabla\rho|}{\rho} \ll q_F; \quad \frac{|\nabla_i \nabla_j \rho|}{|\nabla\rho|} \ll q_F.$$

Making use of invariance relations under uniform displacements and rotations, one arrives at the following form:

$$g[\rho] = g_0(\rho) + g_2^{(2)}(\rho) \nabla\rho \cdot \nabla\rho + \left[g_4^{(2)}(\rho)(\nabla^2\rho)(\nabla^2\rho) + g_4^{(3)}(\rho)(\nabla^2\rho)(\nabla\rho \cdot \nabla\rho) + g_4^{(4)}(\rho)(\nabla\rho \cdot \nabla\rho)^2 \right] + O(\nabla_i^6).$$

The expansion coefficients can be expressed via Taylor expansion coefficients of electronic polarizability $\alpha(q)$.

A formally correct *gradient expansion*

$$E_{XC}[\rho] = \int \rho(\mathbf{r}) \epsilon_{XC}^{LDA}(\rho(\mathbf{r})) d\mathbf{r} + \int B_{XC}(\rho(\mathbf{r})) |\nabla\rho(\mathbf{r})|^2 d\mathbf{r} + \dots \quad (3.60)$$

meets certain problems in its practical implementation:

- the terms of the 4th order and higher in the expansion of the exchange energy diverge;
- the exchange potential diverges already in the 2d order;
- in the 2d order, gradient corrections to exchange energy bring an improvement,

but gradient corrections to correlation energy yield worse results than the LDA.

The last fault can be traced to the fact that the normalization of the XC-density (3.44), valid in the LDA, does not necessarily hold in a truncated gradient expansion (3.60). Particularly, it is violated in what regards the correlation hole (that must integrate to zero around any electron). Therefore, one has to impose necessary constraints, probably using additional gradient terms (nonlinear and not necessarily quadratic) beyond those included in the formal gradient expansion (3.60). These working schemes with explicit nonlinear dependence of the integrand on density and its gradients are referred to as different flavours of *generalized gradient approximation* (GGA)

$$E_{XC}^{GGA}[\rho] = \int \rho(\mathbf{r}) \epsilon_{XC}^{GGA}(\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|, \nabla^2\rho(\mathbf{r})) d\mathbf{r}. \quad (3.61)$$

The parametrization of ϵ_{XC}^{GGA} is chosen so as to satisfy certain limiting cases, like the LDA limit, scaling property $E_X[\rho\lambda] = \lambda E_X[\rho]$ etc.

An example of such arguing was given by Becke²³ who introduced a now broadly used (especially in quantum chemistry applications) form of a GGA approximation to the exchange energy. The correlation was explicitly left out in the Becke analysis, in order to use HF results as a benchmark for tuning this density functional scheme. The asymptotic properties explicitly satisfied were the following: the Coulomb potential of the exchange charge, i.e. of Fermi hole density far from the electron distribution

$$\lim_{r \rightarrow \infty} \int \frac{\rho_X^\sigma(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = -\frac{1}{r}, \quad (3.62)$$

²³A. D. Becke, *Density-functional exchange-energy approximation with correct asymptotic behavior*, Phys. Rev. A **38**, 3098 (1988)

and the exchange energy defined by Eq. (3.27) must behave according to this asymptotic. Moreover, the asymptotic of the spin density is

$$\lim_{r \rightarrow \infty} \rho^\sigma(\mathbf{r}) = e^{-a_\sigma r}, \quad (3.63)$$

where a_σ is a constant related to the ionization potential of the system. The functional form of the exchange energy proposed by Becke guarantees that the density satisfying Eq. (3.63) generates asymptotic potential as in Eq. (3.62):

$$E_X^{(\text{Becke})} = E_X^{\text{LDA}} - \beta \sum_\sigma \int \rho_\sigma^{4/3} \frac{x_\sigma^2}{1 + 6\beta x_\sigma \sinh^{-1} x_\sigma} d\mathbf{r} \quad (3.64)$$

where x_σ is the dimensionless ratio

$$x_\sigma = \frac{|\nabla \rho_\sigma|}{\rho_\sigma^{4/3}}$$

and β is an adjustable parameter, for which Becke proposed, based on least-square fit to Hartree-Fock results over a variety of systems, a value of $\beta=0.0042$ a.u.

A more sophisticated form incorporating both exchange and correlation, that satisfied more essential conditions, has been proposed in 1991 by Perdew and Wang²⁴ for $\epsilon_{\text{XC}}^{\text{GGA}}$ in Eq. (3.61), in terms of ρ and ζ of Eq. (3.32); r_s as related to ρ by Eq. (3.35); $g = [(1+\zeta)^{2/3} + (1-\zeta)^{2/3}]/2$; two differently scaled density gradients $s = |\nabla \rho|/(2\rho k_F)$ and $t = |\nabla \rho|/(2g\rho\sqrt{4k_F/\pi})$, where $k_F = (3\pi^2/\rho)^{1/3}$ is identical to definition of Eqs. (1.7) and (2.35), and many tabulated numerical parameters:

$$\begin{aligned} \epsilon_{\text{XC}}^{(\text{PW91})} &= \epsilon_X + \epsilon_C; \\ \epsilon_X &= \epsilon_X^{\text{LDA}}(\rho, \zeta) \left[\frac{1 + a_1 s \sinh^{-1}(a_2 s) + (a_3 + a_4 e^{-100s^2})s^2}{1 + a_1 s \sinh^{-1}(a_2 s) + a_5 s^4} \right]; \\ \epsilon_C &= \epsilon_C^{\text{LDA}}(\rho, \zeta) + H(\rho, t), \\ H &= \frac{g^3 \beta^2}{2\alpha} \log \left[1 + \frac{2\alpha}{\beta} \frac{t^2 + At^4}{1 + At^2 + A^2 t^4} \right] + C_{c0} [C_c(\rho) - C_{c1}] g^3 t^2 e^{-100g^4 \frac{4}{\pi k_F} t^2}, \\ A &= \frac{2\alpha}{\beta} \left\{ \exp \left[-\frac{2\alpha \epsilon_C^{\text{LDA}}(\rho, \zeta)}{g^3 \beta^2} \right] - 1 \right\}^{-1}, \\ C_c(\rho) &= C_1 + \frac{C_2 + C_3 r_s + C_4 r_s^2}{1 + C_5 r_s + C_6 r_s^2 + C_7 r_s^3}. \end{aligned} \quad (3.65)$$

The inconvenience of having many adjustable parameters in a practical GGA scheme motivated Perdew, Burke and Ernzerhof²⁵ to drop several least important constraints in the formulation of GGA and present a somehow more simplified, as compared to Eq. (3.65),

²⁴J. P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschrig (Academie Verlag, Berlin, 1991), p. 11, reproduced in Perdew *et al.*, Phys. Rev. B **46**, 6671 (1992).

²⁵John P. Perdew, Kieron Burke and Matthias Ernzerhof, *Generalized Gradient Approximation Made Simple*, Phys. Rev. Lett. **77**, 3865 (1996)

and simultaneously more physically transparent scheme. The effect of inhomogeneity of ρ is isolated in the “enhancement factor” F_{XC} , modulating the local exchange:

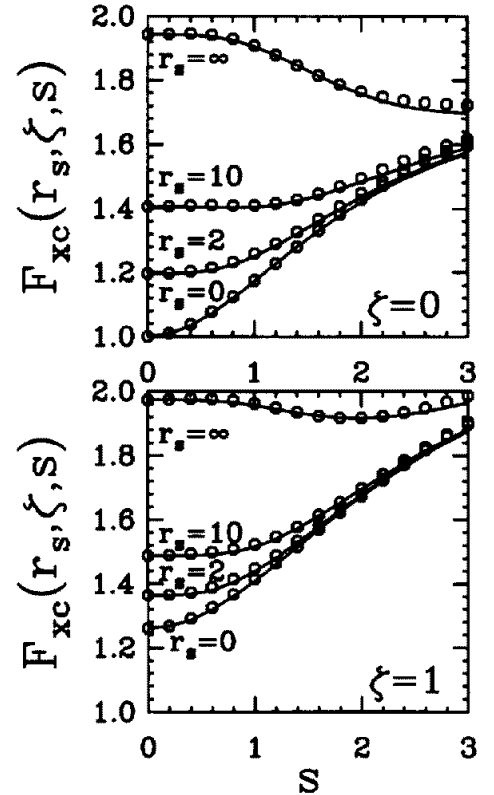
$$E_{XC}^{(PBE)}[\rho^{(+)}, \rho^{(-)}] = \int \rho(\mathbf{r}) \epsilon_X^{\text{unif.}}(\mathbf{r}) F_{XC}(r_s, \zeta, s) dr. \quad (3.66)$$

Whereas the correlation part of $F_{XC}(r_s, \zeta, s)$ is expressible via the function H resembling (but analytically more simple than) that of Eq. (3.65), the exchange part could be mapped onto

$$F_X(s) = 1 + \kappa - \frac{\kappa}{1 + \mu s^2 / \kappa},$$

where $\mu \simeq 0.21951$ and $\kappa = 0.804$ are numerical constants. The figure on the right shows the behaviour of the “enhancement factor” for relevant values of r_s and s in non-polarized and fully polarized cases.

Fig. 1 of Perdew, Burke and Ernzerhof (1996). Enhancement factors F_{XC} showing GGA non-locality. Solid curves denote the PBE results, open circles – those of PW91.



An extensive literature exists on the performance of GGA in different systems, see, e.g., Dal Corso *et al.* (1996).²⁶ Generally, GGA tends to correct to some extent the overbonding that is typical in LDA results. The equilibrium volumes are typically larger according to calculations using GGA, and in many cases agreement with experiment improves. In other cases, the GGA slightly overestimates the volume. Quite important is the inclusion of GGA in the treatment of magnetic systems; one of the most known examples of LDA failures is the hierarchy of energies of different (magnetic and structural) phases of iron, where the LDA wrongly predicts fcc phase to be favourable over the bcc. The inclusion of gradient corrections restores the correct relation between these phases.

²⁶Andrea Dal Corso, Alfredo Pasquarello, Alfonso Baldereschi and Roberto Car, *Generalized-gradient approximations to density-functional theory: A comparative study for atoms and solids*, Phys. Rev. B **53**, 1180 (1996)