Total energy

$$\boxed{\begin{aligned} E[\rho] = {} & \frac{3}{10}(3\pi^2)^{2/3} \int \rho^{5/3}(\vec{r})\,d\vec{r} + \int v(\vec{r})\rho(\vec{r})\,d\vec{r} \\ & + \frac{1}{2}\iint \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}\,d\vec{r}\,d\vec{r}' - \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \int \rho^{4/3}(\vec{r})\,d\vec{r} \\ & + \int \epsilon_c(\rho)\rho(\vec{r})\,d\vec{r} \end{aligned}}$$

approximate

approximate

approximate

How do we determine the density?

Apply the variational principle $\left[\frac{\delta}{\delta\rho}\overbrace{\left\{E[\rho] - \mu\left[\int\rho(\vec{r}) - N\right\}\right.}^{\tilde{E}} = 0\right]$

$$\boxed{\frac{\delta\tilde{G}}{\delta\rho(\vec{r})} = 0 \Rightarrow \frac{1}{2}(3\pi^2\rho)^{2/3} + v(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}\,d\vec{r}' - \left(\frac{3\rho}{\pi}\right)^{1/3} + \frac{\delta E_c}{\delta\rho} = \mu}$$

Interpretation of μ:

$$\int \mu\,\Delta\rho\,d\vec{r} = \int \frac{\delta E}{\delta\rho}\,\Delta\rho(\vec{r}) \Rightarrow \delta E = \mu\,\Delta N$$

$$\boxed{\frac{\delta E}{\delta N}} = \mu$$

μ = Chemical potential / Removal energy

Exercise: Calculate Thomas-Fermi kinetic energy for hydrogen atom density.

Thomas-Fermi theory is expected to be good in high density limit.

Short Coming of Thomas Fermi theory:

① $\mu = 0$ Since $\rho \to 0$ a $r \to 0$ $\Rightarrow \mu = 0$

② No shell structure in the density: Concept of valence shell and therefore all of chemistry / solid-state physics is out

CULPRIT: Approximate treatment of kinetic energy

How to improve kinetic energy: Density gradient is included to improve kinetic energy. For slowly varying densities, perturbation theory gives

$$\Delta T = \frac{1}{72}\int \frac{|\nabla\rho|^2}{\rho}\,d\vec{r}$$

This gives slightly better results but again accuracy is not much. One can then include higher-order corrections.

Give comparison with exact T^0: (Hydrogen-like closed shell atoms)

ATOM	EXACT	$T^{(0)}$	$T^0 + T^{(2)}$
~~He~~			
He	4	3.672 (8.2%)	4.134 (3.4%)
Be	20	17.719 (11.4%)	19.785 (1.1%)
Ne	200	188.849 (5.6%)	202.869 (1.4%)
Mg	304	284.712 (6.3%)	305.978 (0.6)
Ar.	792	737.963 (6.8%)	790.652 (0.2%)

This indicates that it may be possible to write energy exactly in terms of the density for inhomogeneous systems. Is it so? This is when Hohenberg-Kohn theorem comes in

Hohenberg-Kohn theorem:

(i) Ground-state density determines a system uniquely

(a) Proof by Reductio ad absurdum
(b) Proof by Constrained Search. (Page 84)

(ii) Ground state energy can therefore be written as a functional of the density and it is stationary with respect to variations in $\rho(\vec{r})$ at the true density.

$$\rho \rightarrow \Psi \rightarrow H \rightarrow \langle \Psi | H | \Psi \rangle$$

$$\frac{\delta E_v[\rho]}{\delta \rho} = \mu. \quad \left[\begin{array}{l} \text{Interpret } \mu \text{ as chemical potential} \\ \text{and show it to be } -I \text{ or} \\ \qquad -A \end{array} \right]$$

$$\rho \rightarrow \Psi \qquad E[\rho] = \langle \Psi | T + V_{ext} + V_{ee} | \Psi \rangle$$

$$= \int \rho(r) v(\vec{r}) + \underbrace{\langle \Psi[\rho] | T + V_{ee} | \Psi[\rho] \rangle}_{\text{universal functional of the density. in the sense that it is system } [v(\vec{r})] \text{ independent.}}$$

However these functionals are not known. So both $\langle \Psi[\rho] | T | \Psi[\rho] \rangle$ and $\langle \Psi[\rho] | V_{ee} | \Psi[\rho] \rangle$ have to be approximated. We know approximations for T → Thomas-Fermi and beyond. But that is not good enough. Can we treat $T[\rho]$ better

Kohn-Sham Method

This indicates that it may be possible to write energy exactly in terms of the density for inhomogeneous systems. Is it so? This is when Hohenberg-Kohn theorem comes in

Hohenberg-Kohn theorem :

(i) Ground-state density determines ~~the~~ a system uniquely

(a) Proof by Reductio ad absurdum
(b) Proof by Constrained Search. (Page 84)

(ii) Ground state energy can therefore be written as a functional of the density and it is stationary with respect to variations in $\rho(\vec{r})$ at the true density.

$$\rho \to \Psi \to H \to \langle \Psi | H | \Psi \rangle .$$

$$\frac{\delta E_v[\rho]}{\delta \rho} = \mu .$$ [Interpret μ as chemical potential and show it to be $-I$ or $-A$]

$$\rho \to \Psi \qquad E[\rho] = \langle \Psi | T + V_{ext} + V_{ee} | \Psi \rangle$$

$$= \int \rho(r) v(\vec{r}) + \underbrace{\langle \Psi[\rho] | T + V_{ee} | \Psi[\rho] \rangle}_{\text{universal functional of the density. in the sense that it is system } [v(\vec{r})] \text{ independent.}}$$

However these functionals are not known. So both $\langle \Psi[\rho] | T | \Psi[\rho] \rangle$ and $\langle \Psi[\rho] | V_{ee} | \Psi[\rho] \rangle$ have to be approximated. We know approximations for T → Thomas-Fermi and beyond. But that is not good enough. Can we treat $T[\rho]$ better

Kohn-Sham Method,

(34)

Kohn-Sham Method

Assume there exists a system whose ground-state density resembles the true ground-state density i.e

$$\sum_{i} |\phi_i(\vec{r})|^2 = \rho(\vec{r})$$

$$-\frac{1}{2}\nabla^2 \phi_i + v(\vec{r}\,)\,\phi_i = \epsilon_i \phi_i$$

Corresponding Euler equation

$$\frac{\delta T_s[\rho]}{\delta \rho(r)} + v(\vec{r}) = \mu \quad (\mu = \epsilon_{max})$$

Now write the energy of the true system as

$$E[\rho] = \{\langle \Psi | T | \Psi\rangle - T_s[\rho]\} + T_s[\rho]$$
$$+ \int \rho(\vec{r})\, v_{ext}(\vec{r}) + \frac{1}{2}\int \frac{\rho(\vec{r})\,\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\, d\vec{r}\,d\vec{r}\,'$$
$$+ E_{xc}[\rho]$$

$$F[\rho] = \langle \Psi | T | \Psi\rangle + \langle V_{ee}\rangle$$
$$= \langle \Psi | T | \Psi\rangle + \frac{1}{2}\iint \frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\, d\vec{r}\, d\vec{r}\,' + E_{xc}[\rho]$$

$$\frac{\delta E}{\delta \rho} = \frac{\delta T_s[\rho]}{\delta \rho} + \text{the rest} = \mu$$

Equivalent to $-\frac{1}{2}\nabla^2\phi + v_{eff}(\vec{r})\,\phi = \epsilon_i \phi_i$

$\mu = \epsilon_{max}$ by construction

Since we have already seen that $\mu = -I$ or $-A$

$$\epsilon_{max} = -I$$

[Check if our excited state potential $\frac{\delta E_x[\rho]}{\delta \rho_j}$ satisfies Janak's theorem to a good degree.]

(II) Mathematical Derivation of KS equation by Variational principle w.r.to ϕ_i !

(III) Constrained Search for a Kohn-Sham system.

→ Write energy in terms of ϵ_i & ρ here

(If time permits, discuss construction of Kohn-Sham system from exact densities using constrained search).

SOME EXACT RELATIONS FOR KOHN-SHAM THEORY AND EXACT-EXCHANGE KOHN-SHAM THEORY (OPM):

(1) JANAK'S THEOREM:

$$\text{Energy} = \sum n_i \epsilon_i - \frac{1}{2}\int \frac{\rho(\vec r)\rho(\vec r')}{|\vec r-\vec r'|} d\vec r' - \int v_{xc}(\vec r)\rho(\vec r)\, d\vec r + E_{xc}[\rho(\vec r)]$$

$$\begin{aligned}\frac{\partial E}{\partial n_k} = \epsilon_k + \sum n_i\left(\frac{\partial \epsilon_i}{\partial n_k}\right) &- \int \frac{\rho(\vec r)}{|\vec r-\vec r'|}\left(\frac{\partial \rho(\vec r')}{\partial n_k}\right) d\vec r\, d\vec r' \\ &- \int \left(\frac{\partial v_{xc}}{\partial n_k}\right)\rho(\vec r)\, d\vec r \\ &\left.\begin{aligned}&- \int v_{xc}(\vec r)\left(\frac{\partial \rho(\vec r)}{\partial n_k}\right) d\vec r \\ &+ \int \cancel{v_{xc}}\, \underbrace{\frac{\delta E_x}{\delta \rho(r)}}_{v_{xc}} \frac{\partial \rho(\vec r)}{\partial n_k}\, d\vec r\end{aligned}\right\} \overset{\times}{\text{They cancle.}}\end{aligned}$$

$$= \epsilon_k + \sum n_i \frac{\partial \epsilon_i}{\partial n_k} - \int \rho(\vec r)\left\{\frac{\partial}{\partial n_k}(v_{coul} + v_{xc})\right\} d\vec r$$

But $\Delta \epsilon_i = \langle \phi_i | \Delta v_{cal} + \Delta v_{xc} | \phi_i \rangle$

$$\sum_i \frac{\Delta \epsilon_i}{\Delta n_k} = \sum_i \frac{\langle \phi_i | \Delta v_{coul} + \Delta v_{xc} | \phi_i \rangle}{\Delta n_k}$$

$$= \int \rho(\vec r)\, \partial(v_{coul} + v_{xc})\, d\vec r$$

$$\left(\frac{\partial E}{\partial n_k}\right) = \epsilon_k \qquad \text{Janak's theorem}$$

(2) Ionization potential theorem:

Janak's theorem talks about changing 'n_k' thereby considering densities that integrate to non-integer values. What does it mean? Can we define energy functionals for non-integer densities. This is the question one would like to answer

Simple proof:

(I) $\frac{\partial E}{\partial n_k} = \epsilon_k$;

Changing from one ground-state to another

$$\frac{\partial E}{\partial n_k} = \frac{\partial E}{\partial n_{max}} = \epsilon_{max}$$

But $\frac{\partial E}{\partial n_{max}} = -I$ if electrons are being removed

$= -A$ if electrons are being added

$$\Rightarrow \boxed{\epsilon_{max} = -I}$$

Implies that ϵ_{max} remains unchanged during change of electron from N to (N+1)

(II) By construction:

$$\mu_{Kohn-Sham} = \mu_{real}$$

$$\mu_{Kohn-Sham} = +\epsilon_{max} \qquad \mu_{real} = -I$$

$$\boxed{\epsilon_{max} = -I}$$

Rigorous proof

Energy for fractional number of electrons. Since electrons come in full, fractional number can be realized only by statistically mixing ~~the~~ different states.

$$N = M + \Delta = \sum_i i\, p_i \qquad (i = \text{integer}) \quad — ①$$

M = integer

$$E = \sum p_i E_i \qquad E_i \text{ - ground-state energy with } i \text{ electrons.}$$

$$\sum p_i = 1 \quad — ⑪$$

Because of condition ① & ⑪ All p_i's except two of them (Constraint) can be arbitrarily chosen.

$$\delta E = 0 \Rightarrow \sum \delta p_i E_i = 0$$

Also # of electrons & total probability = fixed

$$\sum i\, \delta p_i = 0 \quad — ⓐ \qquad \sum \delta p_i = 0 \quad — ⓑ$$

All "δp_i" can be varied independently except two because of condition ⓐ & ⓑ. Let p_K and p_L be not independent

(One can argue this on the basis of two Lagrange multipliers also)

~~Since~~

$$\delta E = \sum_{i \neq K,L} \delta p_i E_i + \delta p_K E_K + \delta p_L E_L$$

From ⓐ & ⓑ

$$\delta p_K + \delta p_L = -\sum_{i \neq K,L} \delta p_i$$

$$K\,\delta p_K + L\,\delta p_L = -\sum_{i \neq K,L} i\,\delta p_i$$

$$\Rightarrow (L-K)\,\delta p_K = \sum_{i \neq L,K} (i-L)\,\delta p_i \Rightarrow \delta p_K = \sum_{i \neq L,K} \frac{(i-L)}{(L-K)}\,\delta p_i$$

$$(K-L)\,\delta p_L = \sum_{i \neq L,K} (i-K)\,\delta p_i \Rightarrow \delta p_L = -\sum \frac{(i-K)}{(L-K)}\,\delta p_i$$

(38)

⊛ $\delta E = 0$ with arbitrary δp_i

$\Rightarrow E_i = \frac{(L-i)}{L-K} E_K + \frac{(i-K)}{L-K} E_L$ which is

not always true $\Rightarrow \delta p_i = 0$ always & $p_i = 0$ follows

6-1-14 ($\delta p_i = 0$) and p_i being arbitrary is possible only if $p_i = 0$ or $p_i = 1$ because the $\Sigma \delta p_i = 0 \Rightarrow$ some p_i will become negative or greater than 1

So

$$\boxed{\delta E = \sum_{\substack{i \\ \neq K,L}} \left[E_i + \frac{(i-L)}{(L-K)} E_K - \frac{(i-K)}{L-K} E_L \right] \delta p_i}$$

but $p_i = 1$ will give $\Sigma p_i \neq 1 \Rightarrow p_i = 0$ (Some $p_i = 0$ & some $p_i = 1$ are also ruled out because then we can have $\delta p_i \neq 0$ for some with

$$= \sum_{\substack{i \\ \neq K,L}} \frac{1}{(L-K)} \left[(L-K) E_i + (i-L) E_K - (i-K) E_L \right] \delta p_i$$

δp_i transferred from $p_i = 1$ to $p_i = 0$)

5-1-14

$$⊛ \quad = \sum_{\substack{i \\ \neq K,L}} \frac{1}{(L-K)} \left[L(E_i - E_K) - K(E_i - E_L) + i(E_K - E_L) \right] \delta p_i$$

Similarly for the total energy

$$~~\Sigma p~~ \quad p_K + p_L = 1 - \sum_{i \neq K,L} p_i$$

$$K p_K + L p_L = N - \sum_{i \neq K,L} i\, p_i$$

$$(L-K)\, p_K = (L-N) + \sum (i-L)\, p_i$$

$$(K-L)\, p_L = (K-N) + \sum_i (i-K)\, p_i$$

So total energy

$$E(N) = \sum_{i \neq K,L} p_i E_i + \left\{ \frac{(L-N)}{(L-K)} + \sum_i \frac{(i-L)}{(L-K)} p_i \right\} E_K$$

$$- \left\{ \frac{(K-N)}{(L-K)} + \sum_i \frac{(i-K)}{(L-K)} p_i \right\} E_L$$

$$= \frac{(L-N) E_K - (K-N) E_L}{(L-K)}$$

$$+ \frac{1}{\ } \sum \left\{ (L-K) E_i + (i-L) E_K - (i-K) E_L \right\} p_i$$

⊛ otherwise one can get an integer N in between & come up with inconsistency that

$E(N = \text{integer}) = $ sum of energy of other $E(K = \text{integer})$

Since E(N) has to be unique for a given number N all p_i except L & K = 0 otherwise we can generate any energy we like ⇒ E(N) is unique because it is the lowest possible energy

$$\Rightarrow E(N) = \frac{(L-N)E_K + (N-K)E_L}{(L-K)}$$

Then

$$N = \frac{(L-N)}{(L-K)}K + \frac{(N-K)}{(L-K)}L$$

$$\Rightarrow \quad L > N > K$$

Suppose L & K are two faraway integers, then take

$$N = \frac{(L+K)}{2}$$

$$E\left[\frac{L+K}{2}\right] = \frac{1}{2}E_K + \frac{1}{2}E_L \neq E_{\frac{L+K}{2}}$$

So for L & K can't differ from N by more than a fraction⊛. Thus for

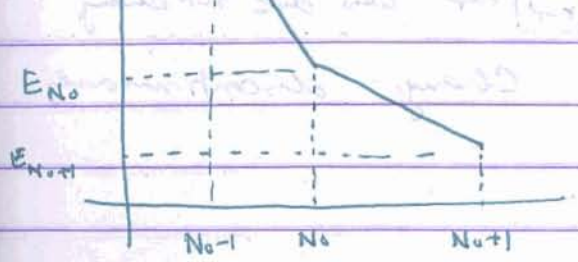
5-1-14

$$N = N_0 + \Delta$$

$$K = N_0 \quad \& \quad L = (N_0+1).$$

$$\Rightarrow \quad \boxed{E(N) = (1-\Delta)E_{N_0} + \Delta E_{N_0+1}}$$

⇒ 5-1-14 This is consistent with the condition that $E(N_0+\Delta) + E(N_0-\Delta) > 2E_{N_0}$ as shown below.



Since in nature it is found that

$$E_{N_0+1} + E_{N_0-1} - 2E_N > 0$$

Also implies that $E(N_0)$ is a minimum with respect to variation w # of elections. To see this

Stability condition. Transfer Δ elections from A_1 to A_2 then

④⓪

$$E(N) = (1-\Delta)E_M + \Delta E_{M+1}$$

$$\frac{\partial E}{\partial N} = \frac{\partial E}{\partial \Delta} = E_{M+1} - E_M = -A \quad \text{for } M < N < M+1$$

$$\frac{\partial E}{\partial N} = \frac{\partial E}{\partial \Delta} = E_M - E_{M-1} = -I \quad \text{for } (M-1) < N < M$$

So μ changes from $-I$ to $-A$ discontinuously as N changes across N.

By Janak's theorem $\boxed{\frac{\partial E}{\partial N} = \epsilon_{max} \rightarrow \epsilon_{max} = -I}$

Demonstrate with the examples of Be and Ne.

CONSEQUENCE OF DISCONTINUOUS CHANGE IN μ FOR THE EXCHANGE-CORRELATION POTENTIAL :

Consider a Hydrogen atom with 1 electron as electron number changes from $(1-\Delta)$ to $(1+\Delta)$ & μ changes from $-I = -13.6$ to ~~A = 0.15 eV~~ $-A = -0.75$ eV. This is a one orbital system

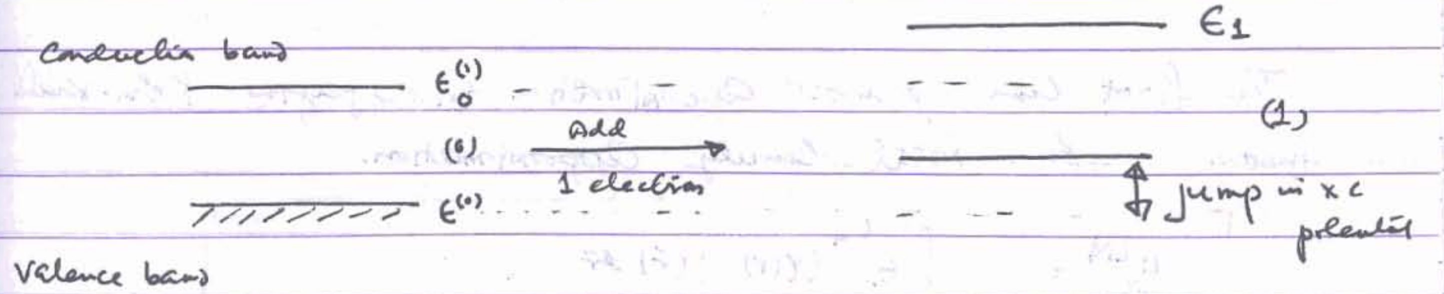
$$-\frac{1}{2}\nabla^2\phi - \frac{\phi}{r} + \phi\int\frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}' + v_{xc}(\vec{r})\phi = \epsilon_m\phi$$

$\phi = \sqrt{\frac{\rho(r)}{2}}$ does not change much as density is changed; $\int \rho(\vec{r}')/|\vec{r}-\vec{r}'|\,d\vec{r}'$ also does not change

$\Rightarrow$ for ϵ_{max} to change discontinuously V_{xc} must jump.

Across an integer $V_{xc}(\vec{r})$ jumps by a constant

Example of a semiconductor or an insulator:



$$\text{Band gap} = I - A$$

$$= -\epsilon_0 - (-\epsilon_1)$$

$$= \epsilon_1 - \epsilon_0$$

$$= \epsilon_0^{(1)} + \Delta - \epsilon_0$$

$$= \underbrace{\left(\epsilon_0^{(1)} - \epsilon_0\right)}_{\text{Kohn-Sham gap}} + \underbrace{\Delta}_{\text{error in S.C. gap}}$$

This concludes lecture 2 (OPM to be done after introducing the LDA)

LECTURE 3

PRACTICAL IMPLEMENTATION OF KOHN-SHAM THEORY

The first and foremost approximation in applying Kohn-Sham theory is the local-density approximation.

$$E_x^{LDA} = \int \epsilon_x^{hom}(\rho(r))\, \rho(\vec{r})\, d\vec{r}$$

$$= -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int \rho^{4/3}(\vec{r})\, d\vec{r}$$

$$\frac{\delta E_x}{\delta \rho(r)} = -\frac{3}{4}\times\left(\frac{3}{\pi}\right)^{1/3}\times\frac{4}{3}\rho^{1/3}$$

$$= -\left(\frac{3\rho}{\pi}\right)^{1/3} = -\left(\frac{k_F}{\pi}\right)$$

$$E_C^{LDA} = \int C\left\{(1+x^3)\ln\left(1+\frac{1}{x}\right)+\frac{x}{2}-x^2-\frac{1}{3}\right\}\rho(\vec{r})\, d\vec{r}$$

$C = -0.0333$, $x = \frac{r_s}{A} = \frac{r_s}{11.4}$ $\quad r_s = \left(\frac{3}{4\pi\rho}\right)^{1/3}$

$$\frac{\delta E_c^{LDA}}{\delta \rho(r)} = -0.0333\ln\left(1+\frac{1}{x}\right)$$

This then is put in the Kohn-Sham equation and it is solved self-consistently.

$$\left[-\frac{1}{2}\nabla^2 + v_{ext} + \int\frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}\,d\vec{r}' + v_{xc}^{LDA}(\rho)\right]\phi_i = \epsilon_i\,\phi_i$$

Results: Energy and highest orbital eigenvalue of some atoms within the LDA

Atom	E^{LDA} (eV)	E^{expt} (eV)	$-\epsilon_{max}$ (eV)	I_{exp} (eV)
H	−12.3	−13.6	6.6	13.6
He	−77.8	−79.0	15.9	25.4
Be	−394.5	−399.1	5.8	9.3
Ne	−3493.9	−3508.1	13.9	21.6
Mg	−5396.8	−5443.2	5.0	7.7
Ar	−14319.7	−14354.6	10.7	15.8

OBSERVATIONS:

(1) LDA is a reasonable approximation as gives energies that are accurate within 5-10%.

(2) ϵ_{max} has large error in it, almost 50% of the exact value.

The observations above, though demonstrated via calculations on atoms, are true in general.

Understanding why the LDA works: Understanding why the energies come out to be accurate in the LDA is done through the Fermi hole. Recall that the energy is given in terms of the hole as

$$E_{xc} = \frac{1}{2}\iint \frac{\rho(\bar{r})\,\rho_{xc}(\bar{r},\bar{r}')}{|\bar{r}-\bar{r}'|}\,d\bar{r}\,d\bar{r}'$$

In the LDA, the exchange correlation hole is replaced by the corresponding expression for the Fermi Coulomb hole

$$E_{xc}^{LDA}[\rho] = \frac{1}{2}\iint \frac{\rho(\bar{r})\,\rho_{xc}^{LDA/HOMOGENEOUS}(\bar{r},\bar{r}';[\rho])}{|\bar{r}-\bar{r}'|}\,d\bar{r}\,d\bar{r}'$$

$$\rho_{x}^{HOM}(\bar{r},\bar{r}') \propto \left(\frac{J_1(k_F(r)\,|\bar{r}-\bar{r}'|)}{k_F(r)\,|r-r'|}\right)^2$$

It is symmetric about the electron position

(I) Both the real hole and the LDA holes satisfy

$$\int \rho_{xc}(\bar{r},\bar{r}')\,d\bar{r}' = -1 \qquad \int \rho_{xc}^{HEG}(\bar{r}\,\bar{r}')\,d\bar{r}' = -1$$

(II) Energy/electron depends on $\int \frac{\rho_{xc}^{LDA}(k_F R)}{R}\,R^2\,dR\,d\Omega_R$

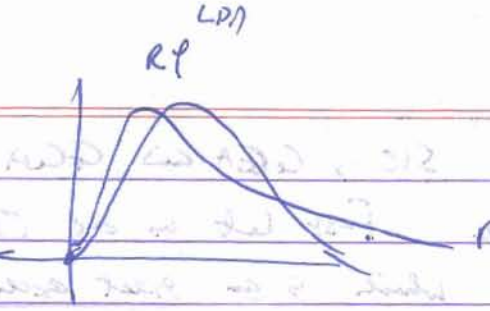
$$= \int R\,\rho_{xc}^{LDA}(k_F R)\,dR\,d\Omega_R$$

$$\int R^2\,\rho_{xc}^{LDA}(k_F R)\,dR\,d\Omega_R = 1 = \int R^2\,\rho_{xc}^{true}(r r')\,d\bar{r}'$$

So $\int R\,\rho_{xc}^{LDA}(k_F R)\,dR\,d\Omega_R$ can be really given much different values from the real hole.

=> Errors within 10%.

(45)

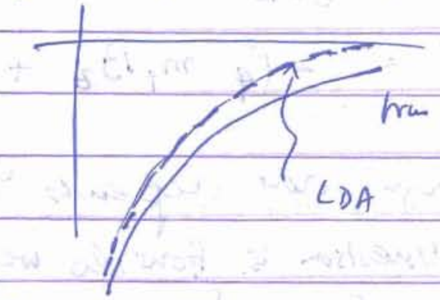


Accuracy of exchange / exchange-correlation hole is important in the accuracy of a functional

<u>Understanding why the LDA does not give good eigenvalues or good band gaps:</u>

This is understood in many different ways, which are all connected with each other

- Potential far away decays as $\exp(-r)$ rather than $-1/r$



This pushes ϵ_{max} up

- For a single electron $\int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}' + E_{xc}^{LDA}[\rho] \neq 0$

As it must. So electron has self interaction that pushes the potential up.

Correcting for asymptotic behaviour or self interaction correction brings energies as well as the eigenvalues much closer to those expected. Because of ~~the~~ self interaction NEGATIVE IONS do not have convergent SCF solutions in the LDA.

<u>Why does the band gap not come out alright?</u>

This is the same reason that the potential does

Going beyond the LDA, SIC, GEA and GGA will be done in the next lecture. First let us do Optimized Potential Model or OPM, which is an exact exchange theory. However before that we do local spin density functional ~~OPTIMIZED POTENTIAL METHOD~~: theory (LSD)

Local Spin Density Functional (LSD):

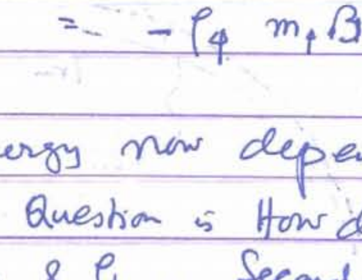
As the name suggests, local spin density functional approximates the energies in terms of local spin density. To motivate this, consider a gas of electrons in a magnetic field B_z coupled only to the spins of the electrons. Then the energy of electrons has an extra term i.e.

$$E = \vec{S}\cdot\vec{B}$$

$$= - \rho_\uparrow m_\uparrow B_z + \rho_\downarrow m_\downarrow B_z$$

So that the energy now depends explicitly on the spin density. Question is How do we express energies in terms of $\rho_\uparrow$ & $\rho_\downarrow$. Second question is does the approximation have to be invoked only when a magnetic field is applied. The answer is that even in general it is a better approximation than regular LDA. It is useful when the number of up and down electrons is different, e.g. in magnetic systems.

Consider electrons so that their numbers are different in ↑ & ↓ states



Consider now the kinetic and exchange energy of such a system

$$KE = \sum_\sigma \sum_i \int \phi^*_{v\sigma} \left(-\tfrac{1}{2}\nabla^2\right) \phi_{v\sigma} \quad \& \quad E_{xc} = -\sum_\sigma \sum_{ij} \int \frac{|\rho_\sigma(r,r')|^2}{\rho|\vec{r}-\vec{r}'|} \, dr\, dr'$$

Each spin contributes its own KE and exchange energy

Write the system, as far as these energies are concerned as

$$\begin{array}{cc} \uparrow & \\ \uparrow & \\ \uparrow & \downarrow \\ \uparrow & \downarrow \\ \uparrow & \downarrow \end{array} \equiv \frac{1}{2} \overbrace{\begin{pmatrix} \uparrow & \downarrow \\ \uparrow & \downarrow \\ \uparrow & \downarrow \\ \uparrow & \downarrow \\ \uparrow & \downarrow \end{pmatrix}}^{\text{spin compensated}} + \frac{1}{2} \overbrace{\begin{pmatrix} \uparrow & \downarrow \\ \uparrow & \downarrow \\ \uparrow & \downarrow \end{pmatrix}}^{\text{spin compensated}}$$

$$\Rightarrow \quad T[\rho_\uparrow \rho_\downarrow] = \tfrac{1}{2} T^{(0)}[2\rho_\uparrow] + \tfrac{1}{2} T^{(0)}[2\rho_\downarrow]$$

$$E_x[\rho_\uparrow \rho_\downarrow] = \tfrac{1}{2} E_x^{(0)}[2\rho_\uparrow] + \tfrac{1}{2} E_x^{(0)}[2\rho_\downarrow]$$

Notice that we can't do the same for correlation energy because correlation energy depends on ~~spin~~ each electron interacting with the other and therefore has ($\uparrow\downarrow$) contribution also.

When we make LSD, we do precisely this. We express the energy of different spins in terms of spin compensated systems

$$T^{LSD}[\rho_\uparrow \rho_\downarrow] = \tfrac{1}{2} T^{LDA}[2\rho^\uparrow] + \tfrac{1}{2} T^{LDA}[2\rho_\downarrow]$$

$$E_x^{LSD}[\rho_\uparrow \rho_\downarrow] = \tfrac{1}{2} E_x^{LDA}[2\rho^\uparrow] + \tfrac{1}{2} E_x^{LDA}[2\rho_\downarrow]$$

How does this change the expression for exchange energy. Let us see that

$$E_x^{LSD}[\rho_\uparrow \rho_\downarrow] = \tfrac{1}{2} E_x^{LDA}[2\rho^\uparrow] + \tfrac{1}{2} E_x^{LDA}[2\rho_\downarrow]$$

$$= \int -\frac{3}{4}\left(\frac{6\rho_\uparrow}{\pi}\right)^{1/3}\rho_\uparrow - \frac{3}{4}\left(\frac{6\rho_\downarrow}{\pi}\right)^{1/3}\rho_\downarrow$$

$$= -\frac{3}{4}\left(\frac{6}{\pi}\right)^{1/3}\int \rho_\uparrow^{4/3}\,d\vec{r} - \frac{3}{4}\left(\frac{6}{\pi}\right)^{1/3}\int \rho_\downarrow^{4/3}\,d\vec{r}$$

The corresponding potentials are

$$v_x^\uparrow = \frac{\delta E_x^{LSD}}{\delta\rho^\uparrow} = -\left(\frac{6\rho_\uparrow}{\pi}\right)^{1/3}$$

$$v_x^\downarrow = \frac{\delta E_x^{LSD}}{\delta\rho_\downarrow} = -\left(\frac{6\cdot\rho_\downarrow}{\pi}\right)^{1/3}$$

We make a similar approximation for the correlation energy. To do so, we first express energy per particle in terms of densities in a slightly different way. We write

$$E_x[\rho^\uparrow \rho^\downarrow] = \int \rho(\vec{r})\, e_x(\rho^\uparrow;\rho^\downarrow)\,d\vec{r}$$

$$\rho = \rho_\uparrow + \rho_\downarrow \quad \& \quad \xi = \frac{\rho^\uparrow - \rho^\downarrow}{\rho^\uparrow + \rho^\downarrow} = \frac{\rho^\uparrow - \rho^\downarrow}{\rho}$$

Then

$$E_x[\rho^\uparrow,\rho^\downarrow] = \frac{1}{2}\int E_x^0[2\rho^\uparrow] + \frac{1}{2}E_x^0[2\rho^\downarrow]$$

from

$$\left.\begin{array}{l}\rho = \rho^\uparrow + \rho_\downarrow \\ \& \ \xi\rho = \rho^\uparrow - \rho^\downarrow\end{array}\right\} \Rightarrow \begin{array}{l}\rho^\uparrow = \rho\dfrac{(1+\xi)}{2} \\ \rho^\downarrow = \rho\dfrac{(1-\xi)}{2}\end{array}$$

So

$$E_x[\rho^\uparrow,\rho^\downarrow] = \frac{1}{2}E_x^0[\rho(1+\xi)] + \frac{1}{2}E_x^0[\rho(1-\xi)$$

$$E_x[\rho^\uparrow\rho_\downarrow] = \frac{1}{2}\times -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\rho^{4/3}(1+\xi)^{4/3}$$

$$+\frac{1}{2}\times -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\rho^{4/3}(1-\xi)^{4/3}$$

$$= \int \rho(\vec{r})\left\{\frac{1}{2}\left(\frac{-3}{4}\right)\left(\frac{3}{\pi}\right)^{1/3}\left\{(1+\xi)^{4/3}+(1-\xi)^{4/3}\right\}\rho^{1/3}\right.$$

$$\epsilon_x(\rho^\uparrow\rho_\downarrow) = \frac{1}{2}\epsilon_x^0(\rho)\left\{(1+\xi)^{4/3}+(1-\xi)^{4/3}\right\}$$

we also know that $\epsilon_x^\uparrow(\rho) = 2^{1/3}\epsilon_x^0(\rho)$

then $\epsilon_x(\rho^\uparrow\rho_\downarrow) = \epsilon_x^0(\rho) \cancel{+\epsilon_x^{(1)}(\rho)+} - \epsilon_x^0(\rho) + \frac{1}{2}\epsilon_x^0\left\{(1+\xi)^{4/3}+(1-\xi)^{4/3}\right\}$

$$= \epsilon_x^{(0)}(\rho) + \frac{1}{2}\epsilon_x^{(0)}\left\{(1+\xi)^{4/3}+(1-\xi)^{4/3}-2\right\}$$

$$\frac{1}{2}\epsilon_x^{(0)} = \left(\epsilon_x^\uparrow(\rho)-\epsilon_x^{(0)}(\rho)\right)C$$

$$= (2^{1/3}-1)\,C\,\epsilon_x^0$$

$$C = \frac{1}{2(2^{1/3}-1)}$$

$$\Rightarrow \epsilon_x(\rho^\uparrow\rho_\downarrow) = \epsilon_x^{(0)}(\rho) + \frac{(\epsilon_x^\uparrow(\rho)-\epsilon_x^0(\rho))}{\cancel{2(2^{1/3}-1)}}f(\xi)$$

$$\boxed{f(\xi) = \frac{(1+\xi)^{4/3}+(1-\xi)^{4/3}-2}{2(2^{1/3}-1)}}$$

It is the same approximation that is made for the correlation energy.

$$\epsilon_c(\rho^\uparrow\rho_\downarrow) = \epsilon_c^{(0)}(\rho) + (\epsilon_c^1(\rho)-\epsilon_c^0(\rho))f(\xi)$$

Comparison of LDA and LSD :

Energy of some atoms in LSD

Atom	E^{LDA} (eV)	E^{LSD} (eV)	E^{expt} (eV)
H	−12.5	−13.4	−13.6
Li	−200.6	−200.9	−203.5
B	−664.2	−664.5	−670.8
N	−1472.84	−1475.95	−1485.3
F	−2700.5	−2700.9	−2713.5
Na	−4397.8	−4398.1	−4414.7
Al	−6572.1	−6572.3	−6594.0
P	−9256.9	−9258.6	−9285.1

BAND-GAPS of some Noble gas atoms

Noble gas	LSD	Expt	E.F
Ne	11.2	21.4	25.4
Ar	8.3	14.2	18.52
Kr	6.8	11.6	—
Xe	5.3	9.2	—

Summarize Lecture 3:

(1) LDA/LSD give reasonably accurate energies

(2) LDA/LSD give 50% eigenenergies

(3) LSD gives about 50% underestimate in band gap of solids

~~The latter two can be~~ of these (2) is due to self-interaction in LDA that gives much faster decaying asymptotic potential

Further band gap underestimate is due to ignorance of derivative discontinuity of the exchange-correlation potential.

In the next lecture we will see how do we go beyond the LDA/LSD.

52

LECTURE 4 (Beyond LDA)

As mentioned earlier, the local-spin-density approximation is the first step towards the development of more accurate functionals. The possible ways of going beyond the LDA are

(1) Self-interaction Correction: We will see that it improves several short-comings of LSD. However it make the potential orbital dependent.

(2) Gradient expansion Approximation (GEA): It was first proposed on the basis of dimensional analysis. Later it was derived on the basis of response theory. It improves energies but not eigenvalues. Asymptotic behaviour of potential is a problem.

(3) GGA (Generalized gradient expansion Approximation): Further imposition of exact conditions on the GEA functionals lead to construction of GGA. These improve the energy substantially. ~~Eigenvalues still~~ Energies come close to chemical accuracy. However, eigenvalues are still a problem.

(4) Meta GGA: Going beyond GGA to include some kinetic energy based terms.

(5) Optimized potential method for exact exchange: This has become quite popular among electronic structure community. Gives exact exchange solutions. ~~Too~~ Is numerically quite cumbersome. Accurate approximations to it that retain its basic ingredients but make computational part easy have been developed. Many

Self-interaction-Corrected LSD (LSD-SIC):

What does self-interaction mean?

Consider hydrogen atom from DFT (Kohn-Sham) point of view

$$\left\{ -\frac{1}{2}\nabla^2 - \frac{1}{r} + V_{\cancel{es}\,\mathrm{Coul}}(\vec{r}) + V_{xc}(\vec{r}) \right\} \phi_1(\vec{r}) = \epsilon_1 \phi_1(\vec{r})$$

Now for a hydrogen atom we know that the equation is

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r}\right) \phi_1 = \epsilon_1 \phi_1$$

$$\Rightarrow \quad \boxed{V_{\mathrm{Coul}}(\vec{r}) + V_{xc}(\vec{r}) = 0}$$

Total energy from DFT point of view

$$E = \cancel{\Sigma\epsilon}\; T + \int -\frac{1}{r}\,\rho(\vec{r})\,d\vec{r} + E_{\mathrm{Coul}} + E_{xc}$$

For hydrogen atom $\boxed{\left(E_{\mathrm{Coul}} + E_{xc}\right) = 0}$

Question: Does the LDA/~~LS~~LSD do that?

Let us check:

LSD $\quad E_x = -\frac{3}{4}\left(\frac{6}{\pi}\right)^{1/3} \rho^{4/3}$

E_c ...

$$E_{\mathrm{Coul}} + E_{xc} > 0$$

Similarly the potential does not cancel exactly with V_{Coul}. Therefore the total energy of the system is not as negative as it should be and the potential is also less binding. This, as pointed out earlier leads to LSD NOT binding negative ions

How to correct for self-interaction?

Self-interaction-correction (SIC) is made by brute-force method.

For each orbital, self-interaction is (ith orbital is considered)

$$E^{SIC}_{i}[\rho_i] = E_{xc}[\rho_i] + \frac{1}{2}\iint \frac{\rho_i(\vec{r})\rho_i(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,d\vec{r}\,' > 0$$

from the total exchange-correlation energy. Subtract this on orbital-by-orbital basis (Perdew-Zunger method)

$$\boxed{E_{xc}^{LSDSIC}[\rho] = \cancel{\Sigma}\, E_{xc}^{LSD} - \sum_{\substack{i\\(occ)}} E_i^{SIC}[\rho_i]}$$

The potential for each orbital is now given as

$$v^{LSDSIC}_{xc,i} = \cancel{v_{xc}}\,\frac{\delta E_{xc}^{LSDSIC}[\rho]}{\delta \rho_i}$$

$$= \cancel{v^{LSDSIC}_{xc}} \int \frac{\delta E_{xc}^{LSD}}{\delta \rho(\vec{r}\,')}\frac{\delta \rho(\vec{r}\,')}{\delta \rho_i(\vec{r})}d\vec{r}\,'$$

$$- \frac{\delta}{\delta \rho_i}\sum_{i\,(occ)} E_i^{SIC}[\rho_i]$$

$$= v_{xc}^{LSD} - v_i^{SIC}[\rho_i]$$

$$v_i^{SIC} = \frac{\delta}{\delta \rho_i}\left[E_{xc}^{LSD}[\rho_i] + \frac{1}{2}\iint\frac{\rho_i(\vec{r})\rho_i(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,d\vec{r}\,'\right]$$

$$= v_{xc}^{LSD}(\rho_i) + \int \frac{\rho_i(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,'$$

Thus

$$v_{xc}^{LSDSIC} = v_{xc}^{LSD}(\rho) - \left(v_{xc}^{LSD}(\rho_i) + \int \frac{\rho_i(\vec{r}\,')}{}d\vec{r}\,'\right)$$

Self-consistent equation in LSDSIC

$$-\frac{1}{2}\nabla^2\phi_i + v_{ext}\phi_i + \int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}'\,\phi_i + v_{xc\,i}^{LSDSIC}\,\phi_i = \epsilon_i\phi_i$$

or $$\left[-\frac{1}{2}\nabla^2 + v_{ext} + \int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}' + v_{xc\,i}^{LSDSIC}\right]\phi_i = \epsilon_i\phi_i$$

Thus in LSDSIC theory, the potential ~~o~~ becomes orbital-dependent. In that sense it is not a conventional Kohn-Sham theory but it works like a charm.

As an example we show electron affinities of some atoms in LSDSIC theory. Keep in mind that the LSD alone does not give ~~so~~ convergent solution for negative ions.

Electron Affinities of some atoms in LSDSIC

ATOM	A^{HF} (eV)	A^{LSDSIC} (eV)	$A^{expt.}$ (eV)
H	−0.3 (unstable)	0.7	0.75
O	−0.5 (unstable)	1.6	1.5
F	1.4	3.6	3.4
Cl	2.6	3.8	3.6

So while HF does not even bind a negative ion or binds them weakly, LSDSIC gives good results for binding of negative ions

NOTE: For extended orbitals, SIC is negligible. Calculations

GRADIENT EXPANSION APPROXIMATION (GEA)

Recall how the gradient correction was made for the kinetic energy for slowly varying densities. This was done by considering the response function and the answer came out to be

$$T[\rho] = T^{TF} + \frac{1}{72}\int \frac{|\nabla\rho|^2}{\rho}\, d\vec{r}$$

In a similar manner, gradient correction to the LDA for exchange was first proposed by Herman et al. on the basis of dimensional analysis

Since $E_x \propto \rho^{4/3}$ $(\propto L^{-4})$, they proposed a correction like

$$\Delta E_x \propto \frac{|\nabla\rho|^2}{\rho^{4/3}} = \frac{L^{-8}}{L^{-4}} = L^{-4}$$

So the first gradient corrected (GEA) exchange energy functional was

$$E_x[\rho] = C_x^{(0)}\int \rho^{4/3}\, d\vec{r} + C_x^{(2)}\int \frac{|\nabla\rho|^2}{\rho^{4/3}}\, d\vec{r}$$

$C_x^{(2)}$ was first determined by fitting exact exchange energies of atoms

Later by analyzing the response function of electron gas (pretty much like what was done for the kinetic energy) Sham derived coefficient $C_x^{(2)}$ analytically. Further improvements by Kleinman & Perdew gave the value

$$C_x^{(2)} = -\frac{7}{[432\pi(3\pi^2)^{1/3}]}$$

This improve the energies quite a lot as the table below shows.

Exchange energies E_x (a.u.) of neutral atoms with non-relativistic HF densities

ATOM	LSD	GEA	EXACT
H	−0.268	−0.294	−0.3125
He	−0.884	−0.970	−1.026
Li	−1.538	−1.675	−1.781
Be	−2.31	−2.50	−2.67
Ne	−11.03	−11.55	−12.11
Ar	−27.86	−28.86	−30.18
Zn	−65.63	−67.36	−69.7
Kr	−88.6	−90.7	−93.9
Xe	−170.6	−173.9	−179.1

Although the GEA for exchange improves energies, it is not without its problems. The functional derivative of E_x^{GEA} is

$$v_x^{GEA} = \frac{\delta E_x^{GEA}}{\delta\rho(\vec{r})} = -\frac{k_F(\vec{r})}{\pi} + C_x^{GEA(2)}\left[\frac{4}{3}\frac{|\nabla\rho|^2}{\rho^{7/3}} - \frac{2\nabla^2\rho}{\rho^{4/3}}\right]$$

Self consistent calculations with the GEA were initially done with a convergence factor multiplying the potential.

The problem of the potential blowing up is a pathology. A similar pathology is seen when we look at the exchange hole in the GEA.

Exchange hole in GEA : Recall that the exact exchange energy can be written in terms of the exchange hole as

$$E_x = \frac{1}{2} \iint \frac{\rho(\vec{r})\, \rho_x(\vec{r},\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\, d\vec{r}\, d\vec{r}\,'$$

where

$$\rho_x(\vec{r},\vec{r}\,') = - \sum_\sigma \frac{|\gamma_\sigma(\vec{r},\vec{r}\,')|^2}{\rho(\vec{r})}$$

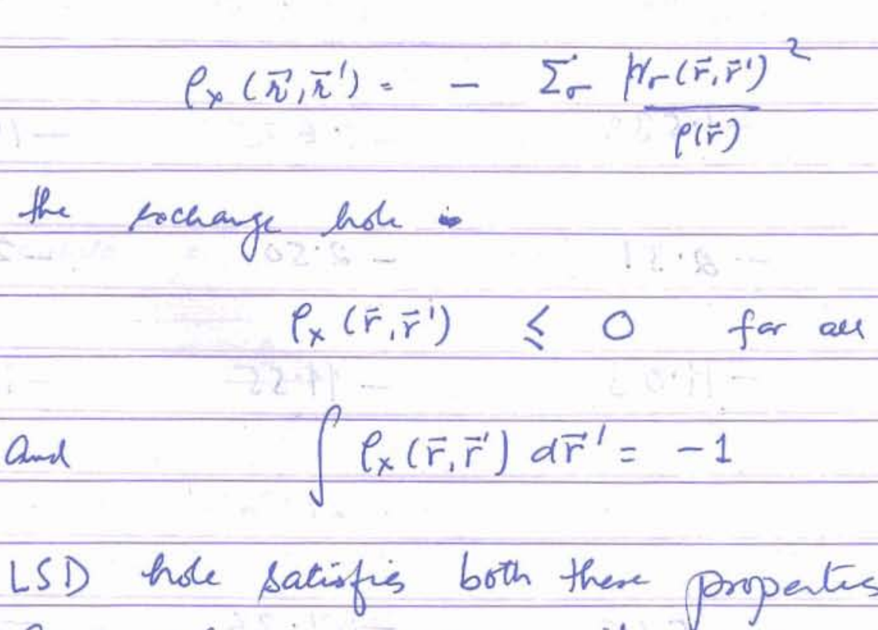
Thus the exchange hole is

$$\rho_x(\vec{r},\vec{r}\,') \leq 0 \quad \text{for all } \vec{r}\,' \qquad (a)$$

And

$$\int \rho_x(\vec{r},\vec{r}\,')\, d\vec{r}\,' = -1 \qquad (b)$$

The LSD hole satisfies both these properties. However when the GEA hole is plotted, it looks like following



The hole has undamped oscillations going up to $|\vec{r}\,'| \to \infty$ for any electron position. Thus the hole violates both (a) and (b) above

To rectify this, Perdew proposed that one chop off all the '+' parts of the hole and also make the hole zero beyond $|\vec{r}\,'-\vec{r}|$ R where R is chosen so that

$$\int_0^R \rho_x(\vec{r},\vec{r}\,')\,\Theta\left[-\rho_x(\vec{r},\vec{r}\,')\right] d\vec{r}\,' = -1$$

And then calculate the exchange energy from the resulting hole. This improved the energies substantially and produced the first Generalized Gradient Expansion Approximation (GGA). Analytic fit to the energy gave

$$E_x^{GGA}[\rho] = C_x^{(0)} \int d\vec{r}\,\rho^{4/3}(\vec{r})\,F^{GGA}(s)$$

When

$$F^{GGA}(s) = \left(1 + 1{\cdot}296\,s^2 + 14\,s^4 + 0{\cdot}2\,s^6\right)^{1/15}$$

where $s = \dfrac{\vec{\nabla}\rho}{2k_F\,\rho}$

[Perdew PRL 55, 1665 (1985); Perdew & Wang PRB 33, 8800(1986)]

The resulting energies are shown below.

ATOM	GEA	GGA	EXACT
H	−0·294	−0·311	−0·313
He	−0·970	−1·033	−1·026
Be	−2·50	−2·68	−2·67
Ne	−11·55	−12·22	−12·11
Ar	−28·86	−30·29	−30·18
Zn	−67·36	−69·93	−69·7
Kr	−90·7	93·8	93·9

Becke's GGA: Becke produced another GGA by imposing another exact condition that the exchange energy density per particle goes as $-\left(\frac{1}{2r}\right)$

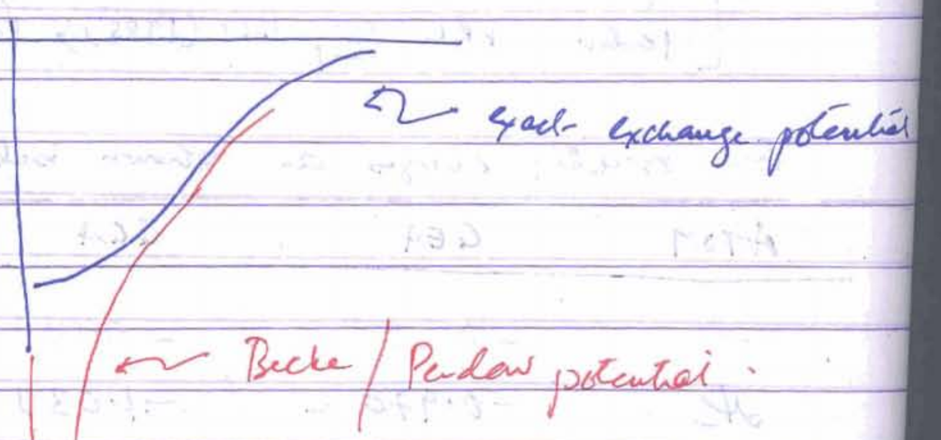
The formula given by him is

$$E_x^{\text{Becke}}[\rho] = E_x^{LSD} - \gamma \int \rho^{4/3} \frac{x}{1+6\gamma \sinh^{-1}(x)}\, dr$$

$$x = \frac{|\nabla \rho|}{(2k_F \rho)} \; ; \; \gamma = .0042$$

Becke functional also gives accurate energies

Although GGA improve the energies tremendously, their potential does not have the correct structure asymptotically (Perdew functional decays exponentially and Becke potential decays as $-\frac{1}{r^2}$) Similarly near the nucleus their behaviour is unlike the exact one



Finally we discuss the optimized potential method (OPM) that has become quite popular, and represents the exact exchange potential.