

1 Outline

1. Not so inhomogeneous electron gas:
 - (a) small amplitude case (linear response) or
 - (b) small wave-vector (slowly varying)
 - (c) How to measure inhomogeneity: s factor
 - i. change in density over range of XC hole.
 - ii. example of Si bond – is it inhomogeneous?
 - iii. can't distinguish our two cases.
2. Linear response (case A)
 - (a) Hohenberg and Kohn section II – read.
 - (b) linear response theory
 - i. *linear* response – the electric polarizability – a response to a small perturbation. (what is “nonlinear” response?)
 - ii. Defining a perturbation – E , ψ , n versus V_{ext} or n_{ext} (perturbed jellium background).
 - iii. Defining a perturbation in *DFT!* E versus change in n . Polarizability as well.
 - iv. Generic idea of the XC kernel – second functional derivative of E_{xc} .
 - (c) Small q limit of linear response (case B too!)
 - i. How to replace an expansion in terms of q with a gradient expansion – the Fourier transform of a derivative.
 - ii. Gradient expansion form generated by linear response theory.
 - iii. Nonanalytic feature in K_{xc} at $2k_F$! Fermi surface problem. Friedel oscillations – effect of sudden change in occupancy at k_F . No problem –at all– if we were not a metal.
3. Gradient expansion (case b)
 - (a) HK part III!
 - (b) General form of a gradient expansion of an energy density. Taylor's series of a functional!
 - (c) Why only rotationally invariant terms count – example of Si crystal that you then rotate.
 - (d) Formal equivalence of $|\nabla n|^2$ and $\nabla^2 n$.

4. Failure of Gradient expansion

(a) What is the effect of the gradients on exchange and correlation?

- i. Cancelling effects:
- ii. make exchange hole deeper and more local (no Friedel stuff, greater confinement of system means more compact orbitals.)
- iii.
- iv. Linear response result – NO minimal to no gradient component to K_{xc} to second order!
- v. Known limiting cases for *high* inhomogeneity:
 - A. $e_c \rightarrow 0$ – the eventual shutdown or freezing of the C energy. Only worry about exchange.
 - B. $E_{xc}[n] \geq 1.8E_x^{LDA}[n]$ – the Lieb-Oxford bound limiting the maximum overall correction to LDA exchange, limiting the net exchange correction.

(b) No such thing as a completely slowly varying system:

- i. Hydrogen atom, and any molecule, or solid surface has s^2 going to infinity at exponential tail of system.
- ii. Cool maps of s^2 and r_s for Si and SiH₄.
- iii. Failure at nuclear cusp where $\nabla^2 n$ goes to infinity. X potential goes to ∞ ! Inability to get rid of $\nabla^2 n$.
- iv. Cool maps of l or s_2 and r_s point out that regions of solids are problems as well, but use of s_1 only does not reveal this.

(c) Consequences of high inhomogeneity:

- i. Lieb-Oxford bound – known limit to net correction due to XC – totally inconsistent with GEA in atom, molecule, etc. XC energy goes to negative ∞ .
- ii. C energy won't go to zero for high homogeneity, it would go to positive ∞ .
- iii. X and C holes derived from gradient expansion do *not* satisfy the known sum rules for each (-1 and 0).

(d) Minor(?) nags – the inconsistency of the gradient expansion.

- i. Inconsistent needs at $s^2 \rightarrow 0$: gradient expansions of X and C energies *do not cancel* as required by linear response! (See high inhomogeneity limit . . .)
- ii. Inconsistent needs at $s^2 \rightarrow 0$: gradient expansion from the homogeneous electron gas does not match that from the heavy atom. Two important Thomas Fermi limits do not agree.
- iii. Even worse intimations of nonanalytic results for certain basic cases – e.g. the slowly varying sinusoidal density (Matthieu gas). Armiento and Mattsson.

5. Resolution of the Problem: the Generalized Gradient expansion.

- (a) The exchange enhancement factor.
- (b) Use of Pade functions to sum gradients to all orders. Good guessing! (κ)
- (c) Unresolved problem – what gradient expansion to use! Solids or finite system? (μ factor, PBE, PBEsol)
- (d) Unresolved problem – what exactly is the LO bound to the *energy density*??

6. A secret weapon – scaling

- (a) The importance of scaling in DFT – the secret weapon.
- (b) Scaling in real systems:
 - i. The isoelectronic series – fixed electrons and nuclear Z varies up to infinity. H^- to Ne^{+8} and beyond.
 - ii. The large atom $N = Z$ fixed, varying to large Z . The periodic table going down a column – noble gases, or C, Si, Ge, Sn.
 - iii. Scaling across a periodic table row – scaling of the 1st, 2nd row atoms e.g. as fill up p shell.
- (c) Definition of uniform scaling to high density:
 - i. Keep our laboratory units fixed, but vary the system.
 - ii. Hydrogenic atom for charge λ .
 - iii. Replacement rules for general case:

$$\begin{aligned} r &\rightarrow \lambda r \\ \psi(\mathbf{r}_1, \dots, \mathbf{r}_N) &\rightarrow \lambda^{3N/2} \psi(\lambda \mathbf{r}_1, \dots, \lambda \mathbf{r}_N) \\ n &\rightarrow \lambda^3 n \end{aligned}$$

defining new system $n_\lambda(\mathbf{r})$ and $\psi_\lambda(\mathbf{r})$ in terms of the old system evaluated at a scaled position.

- (d) How things scale:
 - i. Sanity check: sum rules for n and $|\psi|^2$ don't change.
 - ii. Kinetic energy: $T_\lambda = \lambda^2 T$. Note scaling rule for derivative.
 - iii. Coulomb Potential energy: $U_{ee,\lambda} = \lambda U_{ee}$.
 - iv. Exchange obeys PE scaling! E.g., the LDA exchange form.
 - v. Correlation does not scale (simply)! KE and PE.
- (e) Another scaling law – spin scaling of the exchange energy.
 - i. A complicated way to present a simple fact – the exchange energy and hole only affect electrons of one given spin species at the same time. Relates systems with fixed density and orbitals in one spin species while varying the other.

- ii. Correlation is another matter! A recent model of the correlation hole of the HEG does seem to work.
- (f) Application to GGA:
 - i. Scaling of $r_s - r_s$ defines scaling to high density!
 - ii. Scale invariants: the s_n guys.
 - iii. Constructing a properly scaling exchange energy: The exchange enhancement factor. Simplification of life. Possibly too easy a life? (Multiplication of vast numbers of forms!)
 - iv. Spin scaling adjustments
 - v. Constructing a properly scaling correlation energy – blech! see below ...

7. A long story – correlation energy in the PBE generalized gradient approximation.

- (a) The Thomas-Fermi screening vector k_s . Including the RPA calculation of a point charge screen by an otherwise homogeneous electron gas.
- (b) A different inhomogeneity parameter, t . This measures inhomogeneity relative to k_s , not k_F . A spin-dependence factor $\phi(\zeta)$.
- (c) Correlation does *NOT* scale. It is both KE, which scales as λ^2 and PE, scaling as λ in an indeterminate combination. Note t doesn't scale either.
- (d) Correlation limiting cases, what is known thereof:
 - i. The correlation for the HEG: high r_s expansion and forms fitted to data.
 - ii. The Thomas-Fermi limit – $t \rightarrow 0$, r_s constant, $s \rightarrow 0$. $\epsilon_c = \epsilon_c^{LDA} + \beta\phi^3(\zeta)t^2$. Obviously this requires now the factor β .
 - iii. The high inhomogeneity limit – $t \rightarrow \infty$, or r_s constant and $s \rightarrow \infty$.
 - iv. Uniform scaling to high density, $t = 0$ (or $r_s \rightarrow 0, s = 0$). $\epsilon_c^{LDA} \rightarrow \gamma\phi^3 \ln r_s$. Yet another parameter, γ .
 - v. Uniform scaling to high density, $t \neq 0$ (or $r_s \rightarrow 0, s \neq 0$). $\epsilon_c^{LDA} \rightarrow$ a constant!
- (e) Resolution of these quite conflicting forms into one package: the PBE correlation function.
- (f) Derivation of the PBE correlation function: see my notes.