

How do we know that ∇^2 is Hermitian?

Green's first identity

$$\int_V d^3r u \nabla^2 v = \int_S u \frac{dv}{dn} d\sigma - \int_V d^3r \nabla u \cdot \nabla v$$

Green's second identity

$$\int_V d^3r (u \nabla^2 v - v \nabla^2 u) = \int_S \left(u \frac{dv}{dn} - v \frac{du}{dn} \right) d\sigma$$

$$\int_V d^3r u \nabla^2 v = \int_V d^3r v \nabla^2 u$$

Iff v, u vanish for some surface S bounding V .

Functionals + Functional Derivatives

Functionals are mappings from function spaces to the real (or complex) numbers. A general representation for a functional F is

$$\begin{aligned}
 F[g] = & F_0 + \int dx F_1(x) g(x) + \\
 & + \int dx_1 \int dx_2 F_2(x_1, x_2) g(x_1) g(x_2) \\
 & + \int dx_1 \int dx_2 \int dx_3 F_3(x_1, x_2, x_3) g(x_1) g(x_2) g(x_3) + \dots
 \end{aligned} \tag{1}$$

where the kernels F_i may themselves be either ordinary functions or generalized functions containing, for example, the delta function and its derivatives.

Now let $g = g_0 + \Delta g$. To linear order in Δg we have

$$\begin{aligned}
 F[g] = & F[g_0] + \int dx F_1(x) \Delta g(x) + \\
 & + 2 \int dx_1 \int dx F_2(x_1, x) g_0(x_1) \Delta g(x) \\
 & + 3 \int dx_1 \int dx_2 \int dx F_3(x_1, x_2, x) g_0(x_1) g_0(x_2) \Delta g(x) + \dots
 \end{aligned} \tag{2}$$

(To obtain (2) I have assumed the kernels F_i are symmetric functions of their arguments; This clearly does not restrict the generality of (1))

We can rewrite (2) as

$$F[g_0 + \Delta g] = F[g_0] + \int dx \frac{\delta F[g_0]}{\delta g(x)} \Delta g(x) \quad (3)$$

where

$$\begin{aligned} \frac{\delta F[g_0]}{\delta g(x)} = & F_1(x) + 2 \int dx_1 g_0(x_1) F_2(x_1, x) \\ & + 3 \int dx_1 \int dx_2 g_0(x_1) g_0(x_2) F_3(x_1, x_2, x) \\ & + \dots \end{aligned} \quad (4)$$

Alternatively, when (as is often the case) we do not have an explicit representation such as (1) for F , equation (3) serves to define the functional derivative $\frac{\delta F}{\delta g(x)}$.

The higher functional derivatives are defined by

analogy to (3) :

$$\begin{aligned}
F[g_0 + \Delta g] &= F[g_0] + \int dx \frac{\delta F[g_0]}{\delta g(x)} \Delta g(x) \\
&+ \frac{1}{2} \int dx \int dx' \frac{\delta^2 F[g_0]}{\delta g(x) \delta g(x')} \Delta g(x) \Delta g(x') \\
&+ O(\Delta g)^3
\end{aligned}
\tag{5}$$

From (1) we find an explicit representation for $\delta^2 F / \delta g(x) \delta g(x')$:

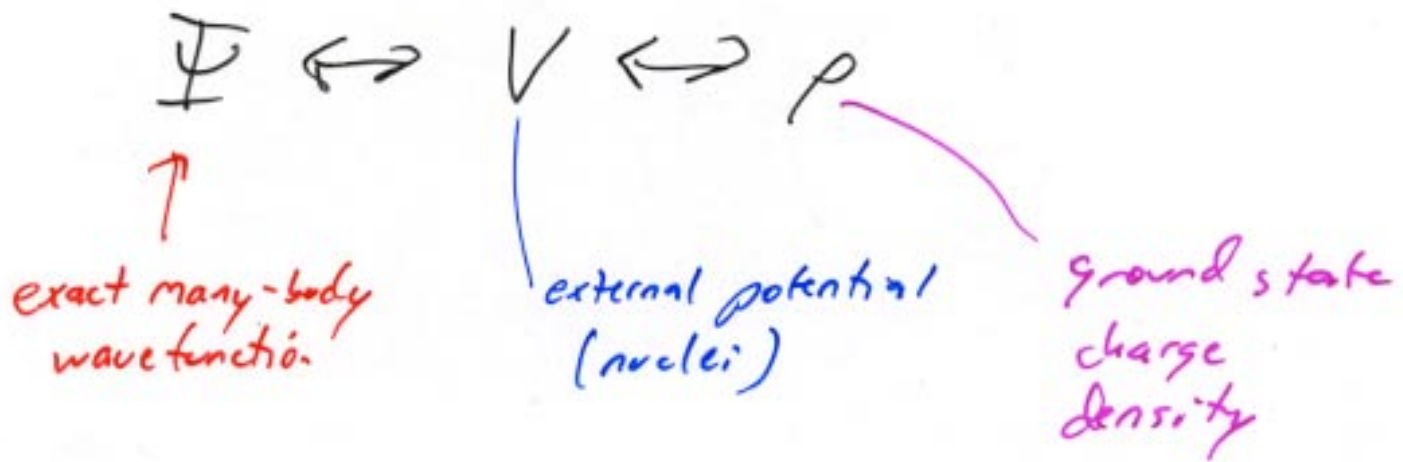
$$\frac{\delta^2 F[g_0]}{\delta g(x) \delta g(x')} = 2F_2(x, x') + 6 \int dx_1 g_0(x_1) F_3(x_1, x, x') + \dots
\tag{6}$$

Example: The Coulomb energy of a charge distribution $n(r)$ is given by a functional $U[n]$, with

$$U_0 = 0, \quad U_1 = 0, \quad U_2(\vec{r}_1, \vec{r}'_1) = \frac{e^2}{2} \frac{1}{|\vec{r}_1 - \vec{r}'_1|}, \quad U_{n \geq 2} = 0$$

$$\frac{\delta U[n_0]}{\delta n(r)} = e^2 \int d^3 r_1 \frac{n_0(\vec{r}_1)}{|\vec{r} - \vec{r}_1|}, \quad \frac{\delta^2 U[n_0]}{\delta n(r) \delta n(r')} = \frac{e^2}{|\vec{r} - \vec{r}'|}$$

Density Functional Theory



All properties of the system are functionals of the charge density, iff there is a one to one correspondence between ρ and V !

Density Functional theory

Hohenberg - Kohn Theorem

Exact:

$$H = \sum_{i=1}^N -\nabla_i^2 + \sum_i v(r_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|}$$

$$\underbrace{\hspace{10em}}_{KE} \quad \underbrace{\hspace{10em}}_V \quad \underbrace{\hspace{10em}}_U$$

$$H\Psi = E\Psi \quad \rho(r) = \langle \Psi^* \Psi \rangle$$

Ψ exact many body wave function

Hohenberg-Kohn Theorem

(1) Can two different v 's give the same ground density $\rho(r)$?

$$v(r) - v'(r) \neq \text{constant}$$

Assume: $\rho'(r) = \rho(r)$

$\Psi' \neq \Psi$ since they solve different Schrödinger's equations

$$\begin{aligned} E' &= \langle \Psi' | H' | \Psi' \rangle < \langle \Psi | H' | \Psi \rangle \\ &= \langle \Psi | H + v' - v | \Psi \rangle \\ &= \langle \Psi | H | \Psi \rangle + \langle \Psi | v' - v | \Psi \rangle \\ &= E + \int d^3r [v'(r) - v(r)] \rho(r) \end{aligned}$$

$$\text{So } \boxed{E' < E + \int d^3r [v'(r) - v(r)] \rho(r)} \quad (1)$$

Now do: $E = \langle \Psi | H | \Psi \rangle < \langle \Psi' | H' | \Psi' \rangle$

$$= E' + \int d^3r [v(r) - v'(r)] \rho(r)$$

$$\boxed{E < E' + \int d^3r [v(r) - v'(r)] \rho(r)} \quad (2)$$

Add (1) and (2): $E + E' < E + E'$ Contradiction!
So $v = v'$ if $\rho = \rho'$ $\Psi \leftrightarrow v \leftrightarrow \rho$

Hohenberg-Kohn, Second Proof (Levy Constrained Search)

$$E = \min_{\Psi} \langle \Psi | H | \Psi \rangle$$

First consider:

$$\min_{\Psi \rightarrow \rho} \langle \Psi | H | \Psi \rangle = \min_{\Psi \rightarrow \rho} \langle \Psi | T + V_{ee} | \Psi \rangle + \int d^3r v(r) \rho(r)$$

because $v(r)$ implies Ψ and thus ρ !

Define: $F[\rho] \equiv \min_{\Psi \rightarrow \rho} \langle \Psi | T + V_{ee} | \Psi \rangle = \langle \Psi^{\min} | T + V_{ee} | \Psi^{\min} \rangle$

Now minimize over all N -electron densities $\rho(r)$

$$E = \min_{\rho} E_{\text{HK}}[\rho] = \min_{\rho} \left\{ F[\rho] + \int d^3r v(r) \rho(r) \right\}$$

Use Lagrange multiplier to fix N :

$$\delta \left\{ F[\rho] + \int d^3r v(r) \rho(r) - \mu \left(\int d^3r \rho(r) \right) \right\} = 0$$

$$\frac{\delta}{\delta \rho(r)} \rightarrow \frac{\delta F[\rho]}{\delta \rho(r)} + v(r) = \mu \quad \text{So } v(r) \leftrightarrow \rho(r)$$

$\rho(r)$ - N -representable any Ψ ?

$\frac{\delta F}{\delta \rho}$ V -representable Ψ and some $v(r)$

Hohenberg-Kohn Theorem #2: Minimum principle

The calculated ground state energy is a minimum for the ground state density $\rho(r)$:

$$\text{Define } F[\Psi] \equiv \langle \Psi | T + U | \Psi \rangle$$

where T :

$$\text{Kinetic energy} = \sum \frac{-\hbar^2 \nabla^2}{2m}$$

$$U: \text{Hartree energy} = \frac{1}{2} \sum_{i,j} \frac{e^2}{|r_i - r_j|}$$

$$\text{since } \Psi = \Psi[\rho], F = F[\rho]$$

$$E_v[\rho] \equiv \int d^3r v(r)\rho(r) + F[\rho]$$

v : external potential

$E_v[\rho]$ is the ground state energy for external potential v for the correct density $\rho(r)$.

$$\text{We know that: } E_v[\Psi] = \langle \Psi | T + V + U | \Psi \rangle$$

$$\delta E_v[\Psi] = 0$$

$$\langle \Psi | \Psi \rangle = 1, N$$

Ground state energy E_v

$$E_v[\Psi'] \equiv \int v(r)\rho'(r)d^3r + F[\rho'] \leftrightarrow E_v[\rho']$$

$$> E_v[\Psi] \equiv \int v(r)\rho(r)d^3r + F[\rho] \leftrightarrow E_v[\rho]$$

$$\text{So: } E_v[\rho'] > E_v[\rho]$$

Kohn-Sham (cont'd)

Non-interacting system:

We do know how to solve:

$$\frac{\delta T_S[\rho]}{\delta \rho(r)} + v_0(r) = \mu \quad (1)$$

for a non-interacting system:

$$[-\nabla^2 + v_0(r)] \psi_i = \epsilon_i \psi_i$$

$$\rho(r) = \sum_{i=1}^{\text{occ}} \psi_i^*(r) \psi_i(r) \quad \begin{array}{l} \text{lowest } N \text{ eigenvalues} \\ \psi_i \text{ single particle orbitals} \end{array}$$

Since this is the correct ground state density $\rho(r)$, it must satisfy (1).

Interacting system:

We want to solve:

$$\frac{\delta T_S}{\delta \rho(r)} + v(r) + v_h(r) + v_{xc}(r) = \mu$$

for $\rho(r)$, but we do not know $\frac{\delta T_S}{\delta \rho(r)}$

But if $v_0 = v + v_h + v_{xc} = v_{\text{eff}}$, we could solve the non-interacting problem:

$$\frac{\delta T_S}{\delta \rho(r)} + v_{\text{eff}} = \mu$$

Kohn-Sham: Self consistent equations for obtaining the ground state properties

Define: $T_s[\rho]$ = kinetic energy of a noninteracting system with density $\rho(r)$

$$E[\rho] = \int v(r)\rho(r)d^3r + T_s[\rho] + \frac{1}{2} \iint \frac{\rho(r)\rho(r')}{|r-r'|} d^3r + E_{xc}[\rho]$$

$$\text{Define: } \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} \equiv v_{xc}(r)$$

$$\text{Now } \frac{\delta E}{\delta \rho(r)} = 0 \text{ for } N[\rho] = \int \rho(r)d^3r$$

Use a Lagrange multiplier:

$$\frac{\delta}{\delta \rho(r)} \left\{ E[\rho] - \mu N[\rho] \right\} = 0$$

$$\text{Define Hartree potential } v_h \equiv \int d^3r' \frac{\rho(r')}{|r-r'|}$$

Then:

$$\frac{\delta T_s}{\delta \rho(r)} + v(r) + v_h(r) + v_{xc}(r) = \mu$$

If $\frac{\delta T_s}{\delta \rho}$ and v_{xc} were known exactly, and were simple functions of ρ , $\rho(r)$ could be found to satisfy this equation.

Local Density Approximation LDA

$$E_{xc}[\rho] = \int d^3r \rho(r) \epsilon_{xc}(\rho(r)) \quad \text{local } \epsilon_{xc}$$

Exchange correlation functional

$$N_{xc} \equiv \frac{\delta E_{xc}}{\delta \rho}$$

$$\epsilon_{xc} = E - T_s - V \rightarrow 0$$

Local Exchange Correlation Functional

kinetic energy for noninteracting electron gas

Total energy for electron gas

Consider $\delta E_{xc}[\rho]$

$$\begin{aligned} E_{xc}[\rho + \delta\rho] - E_{xc}[\rho] &= \int d^3r \delta\rho \frac{\delta E_{xc}}{\delta \rho} + O(\delta\rho^2) \\ &= \int d^3r \left[(\rho + \delta\rho) \epsilon_{xc}(\rho + \delta\rho) - \rho \epsilon_{xc}(\rho) \right] \\ &= \int d^3r \left[\rho \epsilon_{xc}(\rho) + \delta\rho \epsilon'_{xc}(\rho) + \dots \right] + \delta\rho \left[\epsilon_{xc}(\rho) + \dots \right] - \rho \epsilon_{xc}(\rho) \\ &= \int d^3r \left[\delta\rho \rho \epsilon'_{xc}(\rho) + \delta\rho \epsilon_{xc}(\rho) \right] + O(\delta\rho^2) \end{aligned}$$

So we see $N_{xc}^{LDA} = \frac{d}{d\rho} (\rho \epsilon_{xc}(\rho)) \quad \neq \neq$

$$E_x^{LDA}[\rho] = A_x \int d^3r \rho(r)^{4/3} \quad \epsilon_x(\rho) = A_x \rho^{1/3}$$

$$\frac{\delta E_x}{\delta \rho} = N_x = A_x \frac{4}{3} \rho^{1/3}$$

Total Energy Calculations

$$E[\rho] = \int v(r) \rho(r) d^3r + T_s[\rho] + \frac{1}{2} \iint d^3r d^3r' \frac{\rho(r) \rho(r')}{|r-r'|} + E_{xc}[\rho]$$

Now

$$T_s[\rho] + \int d^3r \rho(r) \left\{ v(r) + \int d^3r' \frac{\rho(r')}{|r-r'|} + v_{xc}(r) \right\} = \sum \epsilon_i$$

Two equivalent expressions for the ground state energy for non-interacting (independent) electrons.

So:

$$E[\rho] = \sum \epsilon_i - \frac{1}{2} \int d^3r \frac{\rho(r) \rho(r')}{|r-r'|} + E_{xc}[\rho] - \int \rho(r) v_{xc}(r) d^3r$$

Note: near nuclei there is a very large kinetic energy density and a very negative potential energy density. Extreme accuracy is required.

say 10^{-9} or smaller.

Typical errors

Perdew + Kurth

Atoms, molecules + solids

	LSD	GGA
E_x	5%	0.5%
E_c	100% (too negative)	5%
bond length	1% (too short)	1% (too long)
structure	close packed	more correct
energy barrier	100% (too low)	30% (too low)

Atomization energy for 20 molecules

Unrestricted Hartree Fock	3.1 eV underbinding
LSD	1.3 eV overbinding
GGA	0.3 eV (mostly over)
"Chemical accuracy"	0.05 eV

Exchange and Correlation Energies (general case)

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho]$$

Exact

$$E_x[\rho] = \langle \Phi_{\rho}^{\min} | V_{ee} | \Phi_{\rho}^{\min} \rangle - U[\rho]$$

single
slater determinant
of ground state orbitals

(like Hartree-Fock)

$$e-e \text{ interaction} = \frac{1}{|r_i - r_j|}$$

Hartree energy

$$\iint \frac{\rho(r)\rho(r')}{|r-r'|} d^3r d^3r'$$

Note that: $\langle \Phi_{\rho}^{\min} | T + V_{ee} | \Phi_{\rho}^{\min} \rangle$
 $= T_s[\rho] + U[\rho] + E_x[\rho]$

Correlation

$$E_c[\rho] = F[\rho] - \{T_s[\rho] + U[\rho] + E_x[\rho]\}$$

$$= \langle \Phi_{\rho}^{\min} | T + V_{ee} | \Phi_{\rho}^{\min} \rangle$$

$$- \langle \Phi_{\rho}^{\min} | T + V_{ee} | \Phi_{\rho}^{\min} \rangle$$

$$E_c[\rho] \leq 0$$

positive KE part, negative PG part