## Density Functional Theory: preliminaries

The basic "variable" in density function theory is the electron density:

$$n(\mathbf{r}) = \rho(\mathbf{r}) = N \int \Psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 \dots d\mathbf{r}_N$$

Note we have two symbols.

Let's review this expression. It is the expectation value of the density operator:

$$n(\mathbf{r}) = \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \sum_{i}^{N} \delta(\mathbf{r} - \mathbf{r}_i) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_1 \dots d\mathbf{r}_N$$
  
$$= \int \Psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 \dots d\mathbf{r}_N$$
  
$$+ \int \Psi^*(\mathbf{r}_1, \mathbf{r}, \mathbf{r}_3, \dots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \mathbf{r}, \mathbf{r}_3, \dots, \mathbf{r}_N) d\mathbf{r}_1 d\mathbf{r}_3 \dots d\mathbf{r}_N + \dots$$
  
$$= N \int \Psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 \dots d\mathbf{r}_N$$

#### Density Functional Theory: preliminaries

Let's also review this for a Slater determinant with spin-orbitals:

$$n(\mathbf{r}) = \int \frac{1}{\sqrt{N!}} |\psi_1 \dots \psi_N|^* \sum_{i}^N \delta(\mathbf{r} - \mathbf{r}_i) \frac{1}{\sqrt{N!}} |\psi_1 \dots \psi_N| \, d\mathbf{r}_1 \dots d\mathbf{r}_N$$

First we only do one term of the sum. Let's take i = 1.  $\mathbf{r}_1$  can be argument of all N spin functions (orbitals). For each case, there are (N-1)! ways to permute the N-1 other electron coordinates over the N-1 remaining orbitals (note we integrated over the spin coordinates):

$$\int \frac{1}{\sqrt{N!}} |\psi_1 \dots \psi_N|^* \, \delta(\mathbf{r} - \mathbf{r}_1) \, \frac{1}{\sqrt{N!}} |\psi_1 \dots \psi_N| \, d\mathbf{r}_1 \dots d\mathbf{r}_N$$

$$= \frac{1}{N!} \{\psi_1^*(\mathbf{r})\psi_1(\mathbf{r})(N-1)! + \psi_2^*(\mathbf{r})\psi_2(\mathbf{r})(N-1)! + \psi_3^*(\mathbf{r})\psi_3(\mathbf{r})(N-1)! + \dots\}$$

$$= \frac{(N-1)!}{N!} \sum_{j}^{N} |\psi_j(\mathbf{r})|^2$$
The summation over *i* yields:  $n(\mathbf{r}) = \sum_{j}^{N} |\psi_j(\mathbf{r})|^2 = \sum_{i}^{N} |\psi_i(\mathbf{r})|^2$ 
For closed shell HF:  $n(\mathbf{r}) = 2 \sum_{i}^{N/2} |\phi_i(\mathbf{r})|^2$ 

The basic "variable" in density function theory is the electron density:

$$n(\mathbf{r}) = \rho(\mathbf{r}) = N \int \Psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 \dots d\mathbf{r}_N$$

This is function of the three spatial coordinates (e.g. of x, y and z).

A **functional** is a recipe that has functions as input and yields numbers as output. You put in a function, and get a number out.

Example: Let's have some functions of x, denoted as f(x). The following  $\mathcal{F}$  are functionals:

$$\mathcal{F}[f(x)] = f(2) \ , \ \mathcal{F}[f(x)] = \left. \frac{df(x)}{dx} \right|_{x=2} \ , \ \mathcal{F}[f(x)] = \int_0^{10} |f(x)| \, dx$$

and these are not:

$$\mathcal{F}[f(x)] = 10f(x) + \pi$$
 ,  $\mathcal{F}[f(x)] = \frac{df(x)}{dx}$ 

The two Hohenberg-Kohn theorems are the basis of density functional theory (DFT):

1. The external potential (and hence the ground state energy), is a unique functional of the electron density.

(what is "the external potential?")

2. The functional that delivers the ground state energy of the system, gives the lowest energy if and only if the input density is the true ground state density.

These are (almost) the formulations on wikipedia:

https://en.wikipedia.org/wiki/Density\_functional\_theory, section: Hohenberg-Kohn theorems.

The notes have explicit descriptive explanations.

Let's prove/construct these theorems ....

#### theorem 1

Suppose we have two different external potentials, V and V', for the same ground state (g.s.) density  $n(\mathbf{r})$ . For the normalised g.s. wave functions:

$${m E}=\langle \Psi|H|\Psi
angle$$
 and  ${m E}'=\langle \Psi'|H'|\Psi'
angle$ 

Apply the variational principle twice (at "RR", i.e. Rayleigh-Ritz), and **convert Hamiltonians**. We use:  $H^{(\prime)} = T + W + V^{(\prime)}$ .

$$E \stackrel{\text{RR}}{<} \langle \Psi' | H | \Psi' \rangle = \langle \Psi' | H + \overbrace{V' - V'}^{0} | \Psi' \rangle = \langle \Psi' | H' + V - V' | \Psi' \rangle = E' + \langle \Psi' | V - V' | \Psi'$$
$$E' \stackrel{\text{RR}}{<} \langle \Psi | H' | \Psi \rangle = \langle \Psi | H' + \underbrace{V - V}_{0} | \Psi \rangle = \langle \Psi | H + V' - V | \Psi \rangle = E - \langle \Psi | V - V' | \Psi \rangle$$

Now add:

$$E + E' < E + E' + \langle \Psi' | V - V' | \Psi' 
angle - \langle \Psi | V - V' | \Psi 
angle$$

The densities  $n(\mathbf{r})$  and  $n'(\mathbf{r})$  are identical, and the matrix elements depend on (V, V' and) the density only...

The densities  $n(\mathbf{r})$  and  $n'(\mathbf{r})$  are identical, and the matrix elements depend on (V, V' and) the density only...

$$\langle \Psi | V | \Psi \rangle = \int n(\mathbf{r}) V(\mathbf{r}) \, d\mathbf{r} \, , \, \langle \Psi' | V | \Psi' \rangle = \int n(\mathbf{r}) V(\mathbf{r}) \, d\mathbf{r}$$

So, the matrix elements of V (and of V') cancel. Hence

$$E + E' < E + E'$$

which disqualifies our assumption that V and V' are different.

Now we know  $[n(\mathbf{r})$  is the ground state density]:

 $\overbrace{n(\mathbf{r}) \rightarrow V_{\text{ext}}}^{\text{theorem 1}} \rightarrow \Psi \rightarrow n(\mathbf{r})$ 

Note: this can be generalized to degenerate ground states.

Define a functional:

theorem 2

$$E[\tilde{n}(\mathbf{r})] = \langle \Psi[\tilde{n}] | T + W | \Psi[\tilde{n}] 
angle + \int \tilde{n}(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r}$$

The (fixed) external potential  $V_{\text{ext}}$  is the external potential of the Hamiltonian  $H = T + W + V_{\text{ext}}$  and that yields the g.s. density  $n(\mathbf{r})$  (T and W are the kinetic energy and electron-electron interaction operators).

The function  $\tilde{n}(\mathbf{r})$  can be any charge density. Because of theorem 1 we know it is the g.s. density for the g.s. wave function  $|\Psi[(\tilde{n})]\rangle$  of  $\tilde{H} = T + W + \tilde{V}_{\text{ext}}$ .

For  $\tilde{n}(\mathbf{r}) = n(\mathbf{r})$  we have that  $\tilde{V}_{\text{ext}} = V_{\text{ext}}$  and  $|\Psi[(\tilde{n})]\rangle = |\Psi[(n)]\rangle$  is the g.s. wave function of H. The variational principle says:

 $\langle \Psi[\tilde{n}]|H|\Psi[\tilde{n}]\rangle \geq \langle \Psi[n]|H|\Psi[n]\rangle$ ,

where the equality pertains to the g.s. wave function.

Re-write with the functional:

$$E[\tilde{n}(\mathbf{r})] = \langle \Psi[\tilde{n}]|H|\Psi[\tilde{n}]\rangle \geq \langle \Psi[n]|H|\Psi[n]\rangle = E[n(\mathbf{r})]$$

which is the variational principle for the density functional, i.e. the g.s. density minimizes our functional yielding the g.s. energy for  $V_{\text{ext}}$ .

The first part is often denoted as a functional F.

$$E[\tilde{n}(\mathbf{r})] = \langle \Psi[\tilde{n}] | T + W | \Psi[\tilde{n}] \rangle + \int \tilde{n}(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r}$$
$$= F[\tilde{n}(\mathbf{r})] + \int \tilde{n}(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r}$$

Beautiful: Given the external potential, we know there exists a functional of the density that is minimal for (only) the ground state density. In principle we just need to solve for the density in order to obtain the ground state energy. This is an enormous simplification over wave function methods. We only need the density!

Problematic: but we need to know F... we only know how to get F via the ground state wave function. So no simplification after all? We need another, preferably simple, way to calculate F, directly from the density.

## The Kohn-Sham equations

Both T and W are problematic, but T is most serious... Kohn & Sham "solve" the problem by representing it as non-interacting orbitals (here closed-shell):

$$n(\mathbf{r}) = 2\sum_{i}^{\mathrm{occ}} |\phi_i(\mathbf{r})|^2$$
 so that  $\mathcal{T}^{\mathrm{non-int}}[n(\mathbf{r})] = 2\sum_{i}^{\mathrm{occ}} \langle \phi_i | \frac{p^2}{2m_e} | \phi_i \rangle$ 

 $T^{\text{non-int}}$  is an *approximation* because the real electronic system is not non-interacting, so a correction is needed. The Kohn-Sham orbitals { $\phi_i(\mathbf{r})$ } do *not* make up the real electronic wave function (in principle).

$$F[n(\mathbf{r})] = T^{\text{non-int}}[n(\mathbf{r})] + \frac{e^2}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' + E^{\text{XC}}[n(\mathbf{r})]$$

*F* is the sum of non-interacting kinetic energy, Hartree (Coulomb) energy and exchange-correlation energy.  $E^{\text{XC}}[n(\mathbf{r})]$  has to:

- ▶ repair for the difference between  $T[n(\mathbf{r})]$  and  $T^{\text{non-int}}[n(\mathbf{r})]$  ( $\tilde{E}^{\times C}$ ).
- account for exchange (including self-exchange)
- account for correlation

# The Kohn-Sham equations

Next step: Minimize  $E[n(\mathbf{r})]$  under the constraint of *orthonormal* orbitals. This yields the *Kohn-Sham* equations:

$$\begin{bmatrix} \frac{-\hbar^2}{2m_e} \nabla^2 + V_{\text{ext}}(\mathbf{r}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{XC}}[n(\mathbf{r})] \end{bmatrix} \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$
  
where  $v_{\text{XC}}[n(\mathbf{r})] = \frac{\delta E_{\text{XC}}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$ 

(Kohanoff has a more formal detour)

Note:

- the Lagrange multipliers  $\epsilon_i$  (we took them diagonal),
- the functional derivative in the potential,
- the "double counting" in the Hartree potential,
- the KS equations have to be solved self-consistently, like HF,
- in principle this is easier than HF, if only we knew  $v_{xc}[n(\mathbf{r})]$ ,
- this is similar to the HF eigenvalue equation, it only differs at  $v_{xc}$ .

## The local density approximation

Remember from last week, the exchange energy per particle of the uniform electron gas:

$$\frac{E^{X}}{N} = -\frac{3}{4}e^{2}\sqrt[3]{\frac{3}{\pi}}n^{1/3}$$

Assume that for a *non*-uniform system the exchange energy  $dE^X$  in a volume  $d\mathbf{r}$  with local density  $n(\mathbf{r})$  is the same as that of the uniform electron gas:

$$dE^{X} = (E^{X} \text{ per electron in uniform gas}) \times (\# \text{ electrons in } d\mathbf{r}) = \epsilon_{X}^{\text{LDA}}[n] \times n(\mathbf{r}) d\mathbf{r}$$

This is the essence of the *local density approximation* (LDA), here for the exchange only. We know  $\epsilon_{L}^{\text{LDA}}[n]$  for the uniform electron gas. Inserting and integrating over whole space yields:

$$E_{\text{LDA}}^{\text{X}}[n(\mathbf{r})] = \int \epsilon_{\text{X}}^{\text{LDA}}[n] n(\mathbf{r}) \, d\mathbf{r} = -\frac{3}{4} e^2 \sqrt[3]{\frac{3}{\pi}} \int n(\mathbf{r})^{4/3} \, d\mathbf{r}$$

# The local density approximation

$$E_{\rm LDA}^{\rm X}[n({\bf r})] = -\frac{3}{4}e^2\sqrt[3]{\frac{3}{\pi}}\int n({\bf r})^{4/3}\,d{\bf r}$$

For the potential we need the functional derivative:

$$v_{\rm X}^{\rm LDA} = -e^2 \sqrt[3]{rac{3}{\pi}} n({f r})^{1/3}$$

(note that: 
$$\frac{\partial}{\partial n} \left[ -\frac{3}{4} e^2 \sqrt[3]{\frac{3}{\pi}} n^{4/3} \right] = -e^2 \sqrt[3]{\frac{3}{\pi}} n^{1/3}$$
)

Correlations? How to get  $E^{C}[n(\mathbf{r})]$  in the LDA?

- Start from "numerically exact" results on the uniform electron gas (e.g. quantum Monte Carlo by Ceperly & Alder),
- obtain the corrections w.r.t. "exchange only" LDA, as function of n,
- parametrize the functional [e.g. Perdew & Zunger (1981)].

# The local density approximation

Some remarks:

- The Hartree term has self-interaction. It is imperfectly cancelled by the approximate XC-functional (except for the uniform gas).
- The Fock exchange density is inherently non-local, i.e.  $n_i^X(\mathbf{r}, \mathbf{r}') (= \rho_i^X(\mathbf{r}, \mathbf{r}'))$  depends on two sets of coordinates, so the real DF should connect densties at  $\mathbf{r}$  and  $\mathbf{r}'$  (at least), i.e. should also be non-local. Of course a DF describing the post-HF van der Waals interaction should also be non-local.
- The LDA implicitly assumes a slowly varying charge density. In real systems this often is not true. That it works pretty well nevertheless is not immediately obvious... see later.
- The whole DFT story is based on the variational principle. However, as the LDA (and any other DF you might use) is an approximation to the real DF, it can yield energies *below* real ground state energies.
- DFT is not a wave function method. It is "ab initio" only in so far as the functional is derived from "first-principles".

Another view on XC: the XC hole

$$\begin{split} E_{\text{e-e}} &= \langle \Psi[n] | W | \Psi[n] \rangle = \frac{e^2}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tilde{g}(\mathbf{r}, \mathbf{r}') \, d\mathbf{r} \, d\mathbf{r}' \\ &= \frac{e^2}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' + \frac{e^2}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \left[ \tilde{g}(\mathbf{r}, \mathbf{r}') - 1 \right] \, d\mathbf{r} \, d\mathbf{r}' \\ &= \frac{e^2}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' + \frac{e^2}{2} \int \int \frac{n(\mathbf{r})\tilde{n}_{\text{XC}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' \end{split}$$

 $\tilde{g}(\mathbf{r},\mathbf{r}')$ : el-el pair correlation function (draw!).

$$ilde{g}({f r},{f r}')= ilde{g}({f r}',{f r})$$
 and  $\int ilde{g}({f r},{f r}')n({f r})\;d{f r}=N-1$  (normalization)

 $\tilde{n}_{XC}(\mathbf{r}, \mathbf{r}')$ : exchange-correlation hole.

$$\int n(\mathbf{r}) \left[ \tilde{g}(\mathbf{r},\mathbf{r}') - 1 \right] d\mathbf{r} = \int n(\mathbf{r}) \left[ \tilde{g}(\mathbf{r}',\mathbf{r}) - 1 \right] d\mathbf{r} = \int n(\mathbf{r}') \left[ \tilde{g}(\mathbf{r},\mathbf{r}') - 1 \right] d\mathbf{r}' = \int \tilde{n}_{\mathsf{X}\mathsf{C}}(\mathbf{r},\mathbf{r}') d\mathbf{r}' = -1 \quad , \quad \int \tilde{n}_{\mathsf{C}}(\mathbf{r},\mathbf{r}') d\mathbf{r}' = 0$$

The -1 in N-1 comes from the absence of "self-interaction".

The tildes  $(\tilde{g}, \tilde{n}_{XC})$  have to do with the correction for the kinetic energy. We ignore that aspect here.

Help slide:

When the electrons are far apart  $(|\mathbf{r} - \mathbf{r}'| \rightarrow \infty)$ ,  $E_{e-e}$  is just the energy of the (one-particle) densities iteracting:  $e^2 \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$ 

So  $\tilde{g}(\mathbf{r},\mathbf{r}') = 1$ .

When electrons get closer, they feel each other, Kohanoff: "the probability  $\ldots$  is reduced with respect to finding them at infinite distance", because of Coulomb repulsion (for the same values of the one-electron densities!). So

$$e^{2}rac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}g(\mathbf{r},\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}'\quad ext{with}\quad g(\mathbf{r},\mathbf{r}')<1$$

The energy is reduced compared to the simple Hartree energy.

In fact, the mere presence of exchange only already pushes electrons with like spins apart and makes it impossible for those to be at the same spot simultaneously. So in pure HF:  $g_X(\mathbf{r}, \mathbf{r}) = 1/2$ . The total pair correlation function also accounts for the electron-electron **correlation** (Kohanoff Fig. 2.3):

$$g(\mathbf{r},\mathbf{r}') < g_X(\mathbf{r},\mathbf{r}') < 1$$

The XC energy is:

$$E^{\rm XC} = \frac{e^2}{2} \int n(\mathbf{r}) \left\{ \int \frac{\tilde{n}_{\rm XC}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \, d\mathbf{r}' \right\} d\mathbf{r} \quad \text{with} \quad \tilde{n}_{\rm XC}(\mathbf{r},\mathbf{r}') = n(\mathbf{r}') \big[ \tilde{g}(\mathbf{r},\mathbf{r}') - 1 \big]$$

In the LDA:

$$E_{\text{LDA}}^{\text{XC}}[n(\mathbf{r})] = \int n(\mathbf{r}) \, \epsilon_{\text{XC}}^{\text{LDA}}[n(\mathbf{r})] \, d\mathbf{r}$$

where  $\epsilon_{\text{XC}}^{\text{LDA}}[n(\mathbf{r})]$  is calculated assuming the system is "locally homogeneous", i.e. only determined by  $n(\mathbf{r})$ . This boils down to the LDA approximation of the XC-hole being:

$$\widetilde{n}_{\text{XC}}^{\text{LDA}}(\mathbf{r},\mathbf{r}') = n(\mathbf{r})[\widetilde{g}^{\text{hom}}(|\mathbf{r}'-\mathbf{r}|,n(\mathbf{r}))-1]$$

Here  $n(\mathbf{r}')$  is replaced by  $n(\mathbf{r})$  and the paircorrelation function is that of the homogeneous electron gas at exactly that density. So only the distance  $|\mathbf{r}' - \mathbf{r}|$  matters.

Why does the LDA work? I.e., why isn't it awful, but pretty good (better than HF, but still not good enough for quantum chemists)?

1. We fix **r**,  $\tilde{g}$  is then the g of the uniform electron gas at density  $n(\mathbf{r})$ . This is solved exactly by the LDA, so the xc-hole integrates to -1.

$$\int \tilde{n}_{\mathsf{XC}}(\mathbf{r}',\mathbf{r}) \ d\mathbf{r}' = \int n(\mathbf{r}) [\tilde{g}^{\mathsf{hom}}(\mathbf{r}',\mathbf{r}) - 1] \ d\mathbf{r}' = \int n(\mathbf{r}) [\tilde{g}^{\mathsf{hom}}(|\mathbf{r}'-\mathbf{r}|,n(\mathbf{r})) - 1] \ d\mathbf{r}' = -1$$

note we have  $n(\mathbf{r})$ , not  $n(\mathbf{r}')$ .

2. The exact details of the hole do not matter for the energy, only the spherical average does and that behaves decent.

$$E_{\rm e-e} = \frac{e^2}{2} \int \int \frac{n({\bf r})n({\bf r}')}{|{\bf r}-{\bf r}'|} \, d{\bf r} \, d{\bf r}' + \frac{e^2}{2} \int d{\bf r} \, n({\bf r}) \int \frac{n_{\rm XC}({\bf r},{\bf r}')}{|{\bf r}-{\bf r}'|} \, d{\bf r}'$$

Just do the  $\mathbf{r}'$  integration in spheres centred at  $\mathbf{r}$ , then  $|\mathbf{r} - \mathbf{r}'|$  is constant on the sphere so only the spherical average of the hole matters. Jones & Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989). See Fig. 7, page 703, https://doi.org/10.1103/RevModPhys.61.689

Help slide:

$$\frac{e^2}{2} \int d\mathbf{r} \, n(\mathbf{r}) \int \frac{n_{\mathsf{XC}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' = \frac{e^2}{2} \int d\mathbf{r} \, n(\mathbf{r}) \int \frac{n_{\mathsf{XC}}(\mathbf{r}, \mathbf{r} + \tilde{\mathbf{r}})}{|\tilde{\mathbf{r}}|} \, d\tilde{\mathbf{r}}$$
$$= \frac{e^2}{2} \int d\mathbf{r} \, n(\mathbf{r}) \int_0^\infty \frac{4\pi \tilde{r}^2}{\tilde{r}} \left[ \frac{1}{4\pi \tilde{r}^2} \int_0^{2\pi} \int_0^\pi n_{\mathsf{XC}}(\mathbf{r}, \mathbf{r} + \tilde{\mathbf{r}}) \sin\theta \, d\theta d\phi \right] d\tilde{r}$$

Center the second integral at **r**:  $\tilde{\mathbf{r}} = \mathbf{r}' - \mathbf{r}$ ,  $\tilde{r} = |\tilde{\mathbf{r}}| = |\mathbf{r}' - \mathbf{r}|$ . The volume element in spherical coordinates:  $d\tilde{\mathbf{r}} = \sin \theta \, d\theta d\phi d\tilde{\mathbf{r}}$ 

The red part is the spherical average, centered at **r**. This works because  $1/\tilde{r}$  can be moved outside the angular integral.