

# Supplementary Information: DFT in a Nutshell

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To check you've followed the essay, you should certainly try the conceptual questions here. If you wish to master the material, you should work through the problems. A cheat-sheet is provided at the end for those wishing to check their answers.

## Questions

### Conceptual questions

The following questions are designed as a quick review to see if you digested the basic ideas above well-enough to make deductions on your own. Answers should be verbal or at most one equation.

- 1 Explain why a vibrational frequency is a property of the ground-state of the electrons in a molecule.
- 2 Why is a KS calculation much faster than direct solution of the Schrödinger equation?
- 3 Why is the helium KS potential less deep than the original potential,  $-2/r$ ?
- 4 Is the sum of the KS eigenvalues equal to the total energy?
- 5 What is  $E_{XC}$  for a one-electron system?
- 6 Give the signs of  $E$ ,  $T$ ,  $V_{ee}$ ,  $V$ ,  $U$ ,  $E_X$ , and  $E_C$  for real systems (i.e., atoms, molecules, and solids).

### Pencil and paper problems

The next problems can all be done using the material presented, but each requires taking steps beyond what was explicitly shown in the chapter. They are designed to need only pencil and paper.

- 1 Apply  $F[n] = \langle \Psi | \{ \hat{T} + \hat{V}_{ee} \} | \Psi \rangle$  to the KS system to define  $T_S$  without ever mentioning  $v_S(\mathbf{r})$ . Then prove that  $T \geq T_S$  always.
- 2 Derive  $F[n]$  for a single electron. It has no electron-electron interaction, and is known as the von Weizsäcker kinetic energy.
- 3 Use dimensional analysis to explain the powers of the density in the local approximations of the kinetic energy in 1d and 3d, as well as the exchange energy in 3d.
- 4 Derive a formula for  $E_X[n_\uparrow, n_\downarrow]$  in terms of  $E_X[n]$ , evaluated on various densities. Does the same formula apply to the KS kinetic energy, but with  $E_X$  replaced by  $T_S$ ? How about for  $E_C$ ?
- 5 What is the expectation value of the Hamiltonian ( $\hat{H} = \hat{T} + \hat{V} + \hat{V}_{ee}$ ) evaluated on the KS Slater determinant? Use this to prove that the DFT definition of correlation energy is never positive.
- 6 Write the formula that extracts  $v_S(\mathbf{r})$  from  $n(\mathbf{r})$  for the helium atom. Can you explain why this does *not* tell us the vital  $v_{XC}[n](\mathbf{r})$  for any spin-unpolarized two-electron systems?
- 7 Show that if electrons repelled via a contact repulsion,  $\delta(\mathbf{r} - \mathbf{r}')$ , the exchange is given exactly by LDA, and give its expression, including spin-dependence.

### Computational problems

Finally, we come to calculational problems. In solving these problems, one will greatly be aided by the use of a computer algebra system such as *Mathematica*.

- 1 Calculate the TF kinetic energy for a 1d particle of mass  $m = 1$  in (a) a harmonic well ( $v(x) = x^2/2$ ) and (b) in a delta-well ( $v(x) = -\delta(x)$ ). Give the % errors.
- 2 Evaluate the TF kinetic energy of the H atom and deduce the % error. Repeat using spin-DFT.
- 3 Deduce the exact energy for  $N$  same-spin fermions in a flat box of width 1 bohr. Then evaluate the local approximation to the kinetic energy for  $N = 1, 2$ , and 3, and calculate the % error.

## Answers

### Conceptual questions

- 1 Explain why a vibrational frequency is a property of the ground-state of the electrons in a molecule.  
**Answer:** Within the Born–Oppenheimer approximation, the nuclei move on a potential energy surface (PES) given by the sum of the electronic energy  $E_e(\mathbf{R})$  (found parametrically as a function of the nuclear coordinates,  $\mathbf{R}$ ) and nuclear repulsion energy,  $V_{nn}(\mathbf{R})$ . Vibrational frequencies can then be deduced from the curvature of the PES about the equilibrium nuclear coordinates. Finally, because electronic excitations are negligible at room temperature, the ground-state electronic energy  $E_e^0(\mathbf{R})$  can be used to determine the PES, and thus the vibrational frequencies of a molecule.

- 2 Why is a KS calculation much faster than direct solution of the Schrödinger equation?

**Answer:** A KS calculation only requires solving a non-interacting Schrödinger equation (a 3-dimensional differential equation), though a few iterations to reach self-consistency are required. The direct solution of the interacting Schrödinger equation (a  $3N$ -dimensional differential equation), on the other hand, is extremely expensive and impractical but for small numbers of electrons or systems of low dimensionality.

- 3 Why is the helium KS potential less deep than the original potential,  $-2/r$ ?

**Answer:** Interactions push electrons away from each other and widen the density. Thus for the KS system to mimic the effect of interactions, the KS potential must be less deep.

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#### 4 Is the sum of the KS eigenvalues equal to the total energy?

**Answer:** No. The KS system introduces interactions through a correction to the one-body potential, the Hartree exchange-correlation potential,  $v_{\text{HXC}}[n](\mathbf{r}) = v_{\text{H}}[n](\mathbf{r}) + v_{\text{XC}}[n](\mathbf{r})$ , but because the interactions are two-body effects, the energy of these interactions must be accounted for using the Hartree exchange-correlation energy functional,  $E_{\text{HXC}}[n] = E_{\text{H}}[n] + E_{\text{XC}}[n]$  (or  $E_{\text{H}}[n] = U[n]$ ). The KS eigenvalues only know about the potential, however, and not the energy:

$$\sum_{i=1}^N \varepsilon_i = T_S + V + \int d^3r v_{\text{HXC}}[n](\mathbf{r})n(\mathbf{r}) \quad (1)$$

$$\neq T_S + V + E_{\text{HXC}} = E. \quad (2)$$

For example, the integral over the Hartree potential double-counts the interaction energy:

$$\int d^3r v_{\text{H}}[n](\mathbf{r})n(\mathbf{r}) = 2E_{\text{H}}[n]. \quad (3)$$

Therefore, to obtain the energy from the orbital eigenvalues requires some extra computations. Comparing Eqs. (1) and (2), one obtains:

$$E = \sum_{i=1}^N \varepsilon_i - \int d^3r v_{\text{HXC}}[n](\mathbf{r})n(\mathbf{r}) + E_{\text{HXC}}[n] \quad (4)$$

Thus at the end of the calculation,  $E_{\text{HXC}}[n]$  must be calculated using the self-consistent density  $n(\mathbf{r})$  to obtain the total energy.

#### 5 What is $E_{\text{XC}}$ for a one-electron system?

**Answer:** There is no interaction when there is only one electron, but the Hartree energy  $U[n]$  is always included in a DFT calculation. Therefore for a one-electron system the exchange-correlation energy must cancel the Hartree energy to negate the effect of self-interaction. Thus  $E_{\text{XC}}[n] = -U[n]$ ; specifically  $E_{\text{X}}[n] = -U[n]$  and  $E_{\text{C}}[n] = 0$ .

#### 6 Give the signs of $E$ , $T$ , $V_{\text{ee}}$ , $V$ , $U$ , $E_{\text{X}}$ , and $E_{\text{C}}$ for real systems (i.e., atoms, molecules, and solids).

**Answer:**

- $E < 0$
- $T > 0$
- $V_{\text{ee}} \geq 0$
- $V < 0$
- $U > 0$
- $E_{\text{X}} < 0$
- $E_{\text{C}} \leq 0$

#### Pencil and paper problems

1 Apply  $F[n] = \langle \Psi | \{ \hat{T} + \hat{V}_{\text{ee}} \} | \Psi \rangle$  to the KS system to define  $T_S$  without ever mentioning  $v_{\text{S}}(\mathbf{r})$ . Then prove that  $T \geq T_S$  always.

**Solution:** Considering the KS system, we have  $\hat{V}_{\text{ee}} \rightarrow 0$ . Then

$$F[n] \rightarrow T_S[n] = \min_{\Phi \rightarrow n} \langle \Phi | \hat{T} | \Phi \rangle, \quad (5)$$

where  $\Phi$  is used instead of  $\Psi$  to remind us that a Slater determinant will minimize the non-interacting kinetic energy.

It shall now become obvious that  $T \geq T_S$ .  $T[n]$  is the value when both  $\hat{T}$  and  $\hat{V}_{\text{ee}}$  are minimized for a given density  $n(\mathbf{r})$ , but  $T_S[n]$  is the value when only  $\hat{T}$  is minimized for a given density  $n(\mathbf{r})$ . Therefore  $T[n]$  can never be as small as  $T_S[n]$ , because  $T_S[n]$  minimizes the kinetic energy for a given density.

2 Derive  $F[n]$  for a single electron. It has no electron-electron interaction, and is known as the von Weizsäcker kinetic energy.

**Solution:** Since there is no  $V_{\text{ee}}$ , we simply need to determine  $T[n]$  for one electron with density  $n(\mathbf{r})$ . First, the kinetic energy of an electron with wavefunction  $\phi(\mathbf{r})$  is

$$F[n] \rightarrow T[\phi] = \frac{1}{2} \int d^3r |\nabla \phi(\mathbf{r})|^2. \quad (6)$$

But we can also relate our density directly to the wavefunction; we can take the ground-state electronic eigenfunction to be strictly real, so we have  $n(\mathbf{r}) = \phi(\mathbf{r})^2$ . Then rearranging a little bit:

$$T[\phi] = \frac{1}{2} \int d^3r (\nabla \phi(\mathbf{r}))^2 \quad (7)$$

$$= \frac{1}{2} \int d^3r \frac{(2\phi \nabla \phi)^2}{4\phi^2} \quad (8)$$

Since  $\nabla n = 2\phi \nabla \phi$ , we can rewrite as

$$T^{\text{vW}}[n] = \frac{1}{8} \int d^3r \frac{(\nabla n)^2}{n}, \quad (9)$$

the von Weizsäcker kinetic energy.

3 Use dimensional analysis to explain the powers of the density in the local approximations of the kinetic energy in 1d and 3d, as well as the exchange energy in 3d.

**Solution:** In 3d,  $n \propto 1/L^3$ , where  $L$  is a unit of length, because  $n(\mathbf{r})d^3r$  should be a dimensionless probability. Now kinetic energy scales by  $1/L^2$ , which we can see by considering a one-electron system:

$$T = \frac{1}{2} \int d^3r |\nabla \phi(\mathbf{r})|^2. \quad (10)$$

Since  $|\nabla \phi|^2$  has dimensions  $1/L^5$ , the integration provides  $L^3$ , so we're left with  $1/L^2$  dependence. Therefore

$$T^{\text{TF}} \propto \int d^3r n^{5/3}(\mathbf{r}), \quad (11)$$

in order to give a  $1/L^5$  dependence in the integrand, and a  $1/L^2$  overall dependence.

In 1d,  $n(x) \propto 1/L$ , and kinetic energy still scales by  $1/L^2$ , e.g. the one-electron kinetic energy is

$$T^{1\text{d}} = \frac{1}{2} \int dx \left| \frac{d\phi(x)}{dx} \right|^2, \quad (12)$$

so the integrand in our LDA approximation must have  $1/L^3$  dependence:

$$T^{\text{TF 1d}} \propto \int dx n^3(x), \quad (13)$$

In 3d, the exchange energy scales like  $1/L$  because of the Coulomb potential. To scale in this way, the local approximation to exchange must be:

$$E_X^{\text{LDA}} \propto \int d^3r n^{4/3}(\mathbf{r}). \quad (14)$$

4 Derive a formula for  $E_X[n_\uparrow, n_\downarrow]$  in terms of  $E_X[n]$ , evaluated on various densities. Does the same formula apply to the KS kinetic energy, but with  $E_X$  replaced by  $T_S$ ? How about for  $E_C$ ?

**Solution:** We will soon show the spin-scaling relation,

$$E_X[n_\uparrow, n_\downarrow] = \frac{1}{2}(E_X[2n_\uparrow] + E_X[2n_\downarrow]). \quad (15)$$

In this notation,  $E_X[2n] = E_X[n, n]$  is the expression of the exchange energy as a pure density functional.

First, note that only like spins exchange, so an unpolarized system can be separated into completely polarized parts:

$$E_X[2n] = E_X[n, 0] + E_X[0, n]. \quad (16)$$

Because  $E_X[n, 0] = E_X[0, n]$ , we have that

$$E_X[2n] = 2E_X[n, 0] = 2E_X[0, n]. \quad (17)$$

Now separate  $E_X[n_\uparrow, n_\downarrow]$  into spin components:

$$E_X[n_\uparrow, n_\downarrow] = E_X[n_\uparrow, 0] + E_X[0, n_\downarrow] \quad (18)$$

$$= \frac{1}{2}E_X[2n_\uparrow] + \frac{1}{2}E_X[2n_\downarrow], \quad (19)$$

as desired.

The KS kinetic energy  $T_S$  obeys the exact same spin-scaling relation, because we can again separate out the contributions from each spin:

$$T_S[n_\uparrow, n_\downarrow] = \frac{1}{2}(T_S[2n_\uparrow] + T_S[2n_\downarrow]). \quad (20)$$

However, the correlation energy has no simple spin scaling relation:

$$E_C[n_\uparrow, n_\downarrow] = \text{complicated!} \quad (21)$$

5 What is the expectation value of the Hamiltonian ( $\hat{H} = \hat{T} + \hat{V} + \hat{V}_{ee}$ ) evaluated on the KS Slater determinant? Use this to prove that the DFT definition of correlation energy is never positive.

**Solution:** We want the expectation value of the Hamiltonian evaluated on the KS Slater determinant,  $\Phi$ :

$$\langle \Phi | \hat{H} | \Phi \rangle = T_S + V + U + E_X, \quad (22)$$

since  $\langle \Phi | \hat{V}_{ee} | \Phi \rangle = U + E_X$ . So now consider the variational principle. The true wavefunction  $\Psi$  minimizes the expectation value of  $\hat{H}$ , so the KS expectation should be higher in energy:

$$\langle \Phi | \hat{H} | \Phi \rangle \geq \langle \Psi | \hat{H} | \Psi \rangle = E. \quad (23)$$

Now we can plug in  $E = T_S + V + U + E_X + E_C$  to the RHS of (23), and plug in (22) into the LHS to obtain:

$$T_S + V + U + E_X \geq T_S + V + U + E_X + E_C, \quad (24)$$

which implies that  $E_C \leq 0$ .

6 Write the formula that extracts  $v_S(\mathbf{r})$  from  $n(\mathbf{r})$  for the helium atom. Can you explain why this does not tell us the vital  $v_{XC}[n](\mathbf{r})$  for any spin-unpolarized two-electron systems?

**Solution:** For any spin-unpolarized two-electron system, and supposing there are no magnetic fields (so the ground state KS orbital  $\phi(\mathbf{r})$  can be taken as real), then  $n(\mathbf{r}) = 2(\phi(\mathbf{r}))^2$ , where  $\phi(\mathbf{r})$  is the eigenvector with the lowest eigenvalue of the KS equation,

$$\left\{ -\frac{1}{2}\nabla^2 + v_S(\mathbf{r}) \right\} \phi(\mathbf{r}) = \varepsilon \phi(\mathbf{r}). \quad (25)$$

Therefore we can rearrange and solve for  $v_S(\mathbf{r})$ :

$$v_S(\mathbf{r}) = \frac{\nabla^2 \phi(\mathbf{r})}{2\phi(\mathbf{r})} + \varepsilon. \quad (26)$$

Plugging in  $\phi(\mathbf{r}) = \sqrt{n(\mathbf{r})/2}$  will determine  $v_S(\mathbf{r})$  up to a constant.

However, this will not give us  $v_{XC}(\mathbf{r})$ , unless we also know the external potential  $v(\mathbf{r})$ , since

$$v_{XC}(\mathbf{r}) = v_S(\mathbf{r}) - v(\mathbf{r}) - v_H(\mathbf{r}). \quad (27)$$

If the external potential is known, then the constant  $\varepsilon$  can be determined by using Koopmans' theorem, and thus  $v_{XC}(\mathbf{r})$  can also be determined.

As an aside, if there are magnetic fields, the up and down spin orbitals  $\phi_\sigma(\mathbf{r})$  may in general be different as well as complex. So instead of  $n(\mathbf{r}) = 2(\phi(\mathbf{r}))^2$ , we have  $n(\mathbf{r}) = |\phi_\uparrow(\mathbf{r})|^2 + |\phi_\downarrow(\mathbf{r})|^2$ ; and there is no explicit way to get the phase information to discover the spin-dependent KS potentials,  $v_{S,\sigma}(\mathbf{r})$ .

7 Show that if electrons repelled via a contact repulsion,  $\delta(\mathbf{r} - \mathbf{r}')$ , the exchange is given exactly by LDA, and give its expression, including spin-dependence.

**Solution:** Take the definition of exchange, but replace the Coulomb repulsion by the new delta interaction. The result is:

$$E_X = -\frac{1}{2} \sum_{\substack{\sigma, i, j \\ \text{occ}}} \int d^3r \int d^3r' \delta(\mathbf{r} - \mathbf{r}') \times \quad (28)$$

$$\phi_{i\sigma}^*(\mathbf{r}) \phi_{j\sigma}^*(\mathbf{r}') \phi_{i\sigma}(\mathbf{r}') \phi_{j\sigma}(\mathbf{r}) \\ = -\frac{1}{2} \sum_{\substack{\sigma, i, j \\ \text{occ}}} \int d^3r |\phi_{i\sigma}(\mathbf{r})|^2 |\phi_{j\sigma}(\mathbf{r})|^2. \quad (29)$$

Now take the sums over  $i, j$  inside the integral, because

$$n_{\sigma}(\mathbf{r}) = \sum_j |\phi_{j\sigma}(\mathbf{r})|^2, \quad (30)$$

so

$$n_{\sigma}^2(\mathbf{r}) = \sum_{ij} |\phi_{i\sigma}(\mathbf{r})|^2 |\phi_{j\sigma}(\mathbf{r})|^2. \quad (31)$$

So Eq. (29) becomes

$$E_x = -\frac{1}{2} \sum_{\sigma} \int d^3r n_{\sigma}^2(\mathbf{r}). \quad (32)$$

Thus the exchange energy is in the LSDA form, so LSDA gives the exact exchange energy for a contact repulsion.

As a cool-down exercise, one can also show that Hartree becomes local:

$$U[n] = \frac{1}{2} \int d^3r n^2(\mathbf{r}). \quad (33)$$

### Computational problems

1 Calculate the TF kinetic energy for a 1d particle of mass  $m = 1$  in (a) a harmonic well ( $v(x) = x^2/2$ ) and (b) in a delta-well ( $v(x) = -\delta(x)$ ). Give the % errors.

**Solution:** Recall for a spin-polarized system, the TF kinetic energy is

$$T^{\text{TF 1d}} = \frac{\pi^2}{6} \int dx n^3(x), \quad (34)$$

whereas for one-particle, the exact kinetic energy is

$$T = \frac{1}{2} \int dx \left| \frac{d\phi(x)}{dx} \right|^2, \quad (35)$$

and  $n(x) = (\phi(x))^2$ .

(a) For particle of mass 1 in a harmonic well with a spring constant of 1, the density is

$$n(x) = \frac{1}{\sqrt{\pi}} e^{-x^2}, \quad (36)$$

which produces  $T^{\text{TF}} = 0.302$ . The exact kinetic energy is  $T = 0.25$ , so there is a 21% error.

(b) For a particle in a delta well, the density is

$$n(x) = e^{-2|x|}, \quad (37)$$

which makes  $T^{\text{TF}} = 0.548$ . The exact kinetic energy here is 0.5, so TF makes a 9.6% error.

2 Evaluate the TF kinetic energy of the H atom and deduce the % error. Repeat using spin-DFT.

**Solution:** Recall that for 3d problems, the spin-unpolarized TF kinetic energy is

$$T^{\text{TF}}[n] = a_s \int d^3r n^{5/3}(\mathbf{r}), \quad (38)$$

where  $a_s = 3(2\pi^2)^{2/3}/10 = 2.871$ . For one-electron, we need to spin-scale to get the right result (a one-electron system is a polarized system):

$$T_{\text{pol}}^{\text{TF}}[n] = \frac{1}{2} T^{\text{TF}}[2n] = 2^{2/3} a_s \int d^3r n^{5/3}(\mathbf{r}). \quad (39)$$

The LDA calculation involves the unpolarized  $T^{\text{TF}}$ , whereas the LSDA calculation involves the polarized  $T_{\text{pol}}^{\text{TF}}$ . (LSDA is sometimes meant when LDA is said, because LSDA is a natural extension of LDA and gives more accurate energies.)

For the H atom, the ground-state wavefunction is

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{\pi}} e^{-r}, \quad (40)$$

and  $T = -E = 0.5$ . Putting  $n(\mathbf{r}) = |\psi(\mathbf{r})|^2$  into the LDA and LSDA TF gives 0.289 and 0.459, respectively, with errors of -42% and -8%. Now we can see why people use LSDA!

3 Deduce the exact energy for  $N$  same-spin fermions in a flat box of width 1 bohr. Then evaluate the local approximation to the kinetic energy for  $N = 1, 2$ , and 3, and calculate the % error.

**Solution:** Considering the well from  $x = 0$  to  $x = 1$ , we have eigenfunctions

$$\phi_j(x) = \sqrt{2} \sin j\pi x \quad (41)$$

with energies

$$\varepsilon_j = \frac{\pi^2 j^2}{2}. \quad (42)$$

Therefore the exact energy of a system with  $N$  non-interacting particles (same-spin) will be

$$E = \sum_{j=1}^N \varepsilon_j = \frac{\pi^2}{6} N(N+1)(N+\frac{1}{2}). \quad (43)$$

The density will be

$$n(x) = \sum_{j=1}^N |\phi_j(x)|^2. \quad (44)$$

Again using (34), we obtain Table 1.

Table 1. Exact and TF energies for $N$ particles in a box.			
$N$	$E$	$E^{\text{TF}}$	% error
1	4.935	4.112	-17%
2	24.67	21.80	-12%
3	69.09	62.92	-8.9%

An intriguing question is: why does TF underestimate the kinetic energy of a particle in a box, but overestimate for the harmonic oscillator and  $\delta$ -well?