The e-e cusp and DFT

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Post-HF methods I

We have looked at three kinds of post-Hartree–Fock methods:

- Configuration Interaction (CI): Variational. Full CI is exact but scales exponentially. Truncated CI (e.g. CISD) not size-consistent.
- Coupled-cluster (CC): Also potentially exact. Truncated methods are size-consistent. CCSD(T) is the method of choice if you can afford the $\mathcal{O}(N^7)$ computational cost.
- Møller–Plesset Perturbation Theory (MPn): Perturbation theory starting from HF reference state. Usually only used at second-order: MP2. Known to diverge. MP2 is the first term to include correlation (MP0 and MP1 are parts of the HF energy).

Post-HF methods II

Practical considerations: CI, CC and MP2 are expensive!

Method	Cost	Description
HF	N^4	Starting point for correlated methods.
MP2	N^5	OK. Useful for optimizations.
CISD	N^6	Not size-consistent.
CCSD(T)	N^7	Very accurate.

All correlated methods require large basis sets with high angular functions.

The electron–electron cusp I

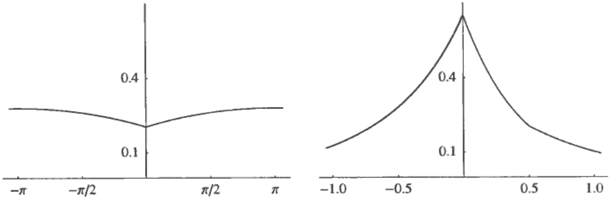


Fig. 7.5. The electronic and nuclear cusps of the ground-state helium atom with one electron fixed at a position $0.5a_0$ from the nucleus (atomic units). On the left, the wave function is plotted on a circle of radius $0.5a_0$ centred at the nucleus; on the right, the wave function is plotted along the axis through the nucleus and the fixed electron.

Correlation is the description of this kink.

All figures from "Molecular Electronic Structure Theory" by Helgaker, Jorgensen and Olsen

The electron–electron cusp II

Principle and partial wave expansions.

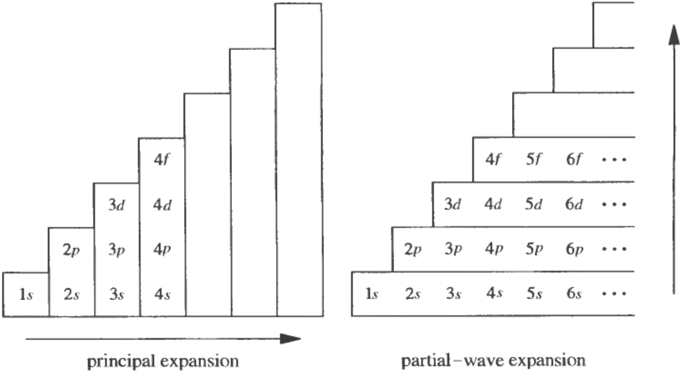
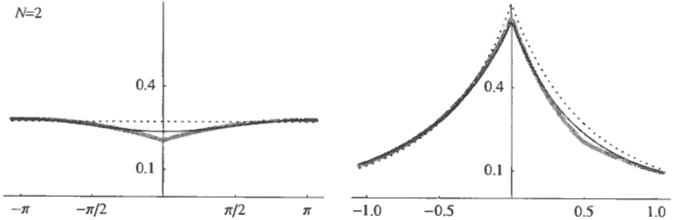


Fig. 7.9. The principal and partial-wave expansions.

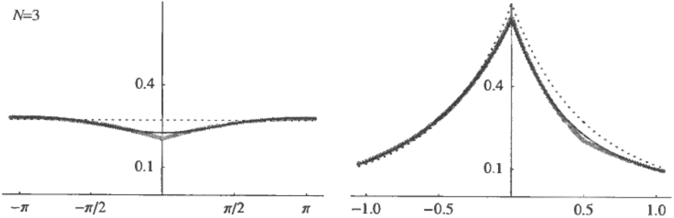
The electron–electron cusp III

He_2: Principle wave expansion with one electron fixed at 0.5Å:
$n = 2$



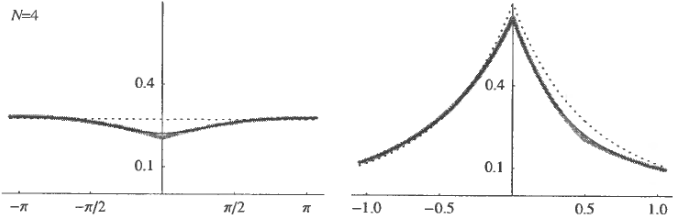
The electron–electron cusp IV

He$_2$: Principle wave expansion with one electron fixed at 0.5Å: $n = 3$



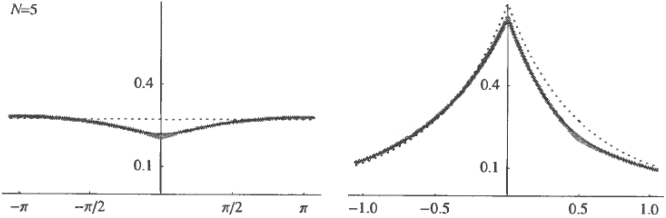
The electron–electron cusp V

He_2: Principle wave expansion with one electron fixed at 0.5Å: $n = 4$



The electron–electron cusp VI

He_2: Principle wave expansion with one electron fixed at 0.5Å: $n = 5$



These cusps make correlation hard. Not only do the methods scale poorly with size, but we need rather large basis sets to get sensible results.

Density-Functional Theory I

Hohenberg & Kohn (Phys. Rev. B, **136**, 864 (1964)):

Theorem

H–K Theorem 1 There is a one-to-one mapping between the electronic density and the external potential, and hence, the Hamiltonian:

$$\rho(\mathrm{r}) \iff \mathcal{H}$$

Proof is by *reductio ad absurdum*.

Density-Functional Theory II

Consider the Hamiltonian with the electron–nuclear potential v_{ext} (this is sometimes called the *external* potential):

$$\mathcal{H} = -\frac{1}{2}\sum_{i}^{N}\nabla_i^2 + \sum_{i<j}\frac{1}{r_{ij}} + \sum_{i}^{N} v_{\mathrm{ext}}(\mathrm{r_i}) \quad (1)$$

- We already know that $\mathcal{H}$ determines $\rho(\mathrm{r})$.
- Let v_{ext}^{1} and v_{ext}^{2} arise from the same density.
- We therefore have two Hamiltonians $\mathcal{H}_1$ and $\mathcal{H}_2$ with the same ground state density but with *different* ground state wavefunctions, Ψ_1 and Ψ_2.

Density-Functional Theory III

- Consider $\mathcal{H}_1$: The variational principle states that

$$\begin{aligned} E_0^1 < \langle \Psi_2 | \mathcal{H}_1 | \Psi_2 \rangle &= \langle \Psi_2 | \mathcal{H}_2 | \Psi_2 \rangle + \langle \Psi_2 | \mathcal{H}_1 - \mathcal{H}_2 | \Psi_2 \rangle \\ &= E_0^2 + \langle \Psi_2 | v_{\mathrm{ext}}^1 - v_{\mathrm{ext}}^2 | \Psi_2 \rangle \\ &= E_0^2 + \int \rho(\mathrm{r}) \left[v_{\mathrm{ext}}^1(\mathrm{r}) - \mathrm{v}_{\mathrm{ext}}^2(\mathrm{r}) \right] d\mathrm{r} \end{aligned}$$

- Similarly $E_0^2 < E_0^1 + \int \rho(\mathrm{r}) \left[v_{\mathrm{ext}}^2(\mathrm{r}) - \mathrm{v}_{\mathrm{ext}}^1(\mathrm{r}) \right] d\mathrm{r}$
- Adding the inequalities:

$$E_0^1 + E_0^2 < E_0^2 + E_0^1 \quad \rightarrow\leftarrow$$

- Hence $\rho(\mathrm{r}) \iff \mathcal{H}$

Density-Functional Theory IV

Pause!

External potential: What is $v_{\mathrm{ext}}(\mathrm{r})$? It is a one-electron *multplicative* (i.e., not differential) operator that will normally be the electron–nuclear interaction. But it could just as well include, say, the interaction with an external field.

Q:

Show that for a many-electron wavefunction,

$$\langle \Psi | v_{\mathrm{ext}} | \Psi \rangle = \int \rho(\mathrm{r}) \mathrm{v}_{\mathrm{ext}}(\mathrm{r}) \mathrm{dr}.$$

Hint: use the definition of the density used in the H_2 lecture notes. Also, keep in mind that v_{ext} is a spin-free, one-electron operator.

Density-Functional Theory V

Edgar Bright Wilson's observation: To know the Hamiltonian we need to know the number of electrons and position and charge of the nuclei. These can be obtained from the density:

- $N = \int \rho(\mathrm{r})\mathrm{dr}$
- Position and charge of nuclei can be obtained from the cusps:

$$\frac{\partial}{\partial r}\langle\rho(r)\rangle_{\mathrm{sph}}\bigg|_{r=0} = -2Z\langle\rho(0)\rangle_{\mathrm{sph}}$$

So ρ completely determines the Hamiltonian and therefore the ground-state energy (and also all excited state energies!).

Density-Functional Theory VI

What the Hohenberg–Kohn theorem allows us to do is (formally) write the energy as a *functional* of the density.

$$\begin{aligned} E = E[\rho] &= T[\rho] + V_{\mathrm{ee}}[\rho] + V_{\mathrm{en}}[\rho] \\ &= F[\rho] + \int \rho(\mathrm{r}) \mathrm{v}_{\mathrm{ext}}(\mathrm{r}) \mathrm{dr} \end{aligned}$$

This leads to the second Hohenberg–Kohn theorem:

Theorem

H–K Theorem 2 If $\tilde{\rho}$ is an approximate density then

$$E[\rho] \leq E[\tilde{\rho}]$$

Density-Functional Theory VII

This is how the theorem arises:

- From the previous theorem, we know that $\tilde{\rho}$ determines its own unique potential $\tilde{v}_{\rm ext}$, the Hamiltonian $\tilde{\mathcal{H}}$, and hence the ground state wavefunction $\tilde{\Psi}$: $\tilde{\rho} \rightarrow \tilde{v}_{\rm ext} \rightarrow \tilde{\mathcal{H}} \rightarrow \tilde{\Psi}$.
- We can now use this wavefunction $\tilde{\Psi}$ as a trial wavefunction for a Hamiltonian $\mathcal{H}$ with external potential $v_{\rm ext}$:
- Using the variational principle

$$E_0 \equiv E[\rho] \leq \langle\tilde{\Psi}|\mathcal{H}|\tilde{\Psi}\rangle = F[\tilde{\rho}] + \int \tilde{\rho}(\mathrm{r})\mathrm{v}_{\rm ext}(\mathrm{r})\mathrm{dr} = \mathrm{E}[\tilde{\rho}]$$

That is, for any trial density $\tilde{\rho}$, $E[\rho] \leq E[\tilde{\rho}]$.

So *in principle* we can search over all N-electron densities to find the one that leads to the lowest energy.

Density-Functional Theory VIII

Look at this another way: Consider the minimization procedure in two steps:

$$\begin{aligned}
E_0 &= \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{\mathrm{ee}} + v_{\mathrm{ext}} | \Psi \rangle \\
&= \min_{\rho} \left(\min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{V}_{\mathrm{ee}} + v_{\mathrm{ext}} | \Psi \rangle \right) \\
&= \min_{\rho} \left(\min_{\Psi \to \rho} \left[\langle \Psi | \hat{T} + \hat{V}_{\mathrm{ee}} | \Psi \rangle + \int v_{\mathrm{ext}}(\mathrm{r}) \rho(\mathrm{r}) \mathrm{d}\mathrm{r} \right] \right)
\end{aligned}$$

In the second line the inner minimization is constrained to all wavefunctions that give $\rho(\mathrm{r})$, while in the outer minimization this condition is removed by searching all $\rho(\mathrm{r})$.

Density-Functional Theory IX

The term in the square brackets is the functional $F[\rho]$, therefore

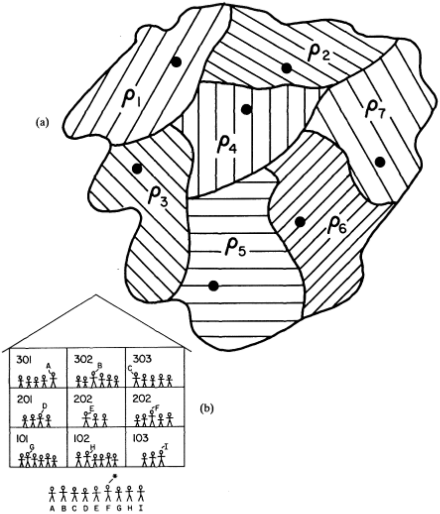
$$\begin{aligned} E_0 &= \min_{\rho} \left(F[\rho] + \int v_{\mathrm{ext}}(\mathrm{r})\rho(\mathrm{r})\mathrm{d}\mathrm{r} \right) \\ &= \min_{\rho} E[\rho] \end{aligned}$$

where

$$E[\rho] = F[\rho] + \int v_{\mathrm{ext}}(\mathrm{r})\rho(\mathrm{r})\mathrm{d}\mathrm{r}$$

This double-step minimization is illustrated in the following figure (from Parr and Yang, *Density-Functional Theory*).

Density-Functional Theory X



Density-Functional Theory XI

In practice searching over all N-electron densities is next to impossible. How do we do this? If we are given a trial N-electron density $\tilde{\rho}$, how can we obtain the corresponding external potential $v_{\rm ext}$? This can be done for a one or two electron system (Ex. How?) but not in general.

All this would have been a curiosity had it not been for a paper by Kohn & Sham published in 1965 (Phys. Rev. A **140**, 1133) which gave us what we now know as Kohn–Sham DFT.

But before getting to Kohn–Sham DFT, let's look at a couple of other attempts at formulating a density-functional theory...

Thomas–Fermi Theory I

In 1927 Enrico Fermi and Llewellyn Thomas developed the first true density functional for the energy. In 1928, P. A. M. Dirac modified the TF model to include the effects of exchange. This TFD model turned out to be poorer than the original model. As we shall see, the beauty of the TF/TFD models is their simplicity. However, they proved to be not so accurate, and, in particular, could not describe chemical bonding. So what's their use? These models, as precursors to modern DFT, contain ideas that will form the basis of the density functionals we use today.

We will develop a quick and elegant derivation of the TFD model here, at the expense of mathematical rigour.

First we re-visit **uniform scaling of the electronic coordinates...**

Thomas–Fermi Theory II

Theorem

Under uniform scaling of the electronic coordinates:

$$r_i \to \alpha r_i,$$
$$\psi(r_i) \to \psi_\alpha(r_i) = \alpha^{3N/2}\psi(\alpha r_i).$$

This form of the scaling is needed to ensure normalization.

Q: Show that $\rho_\alpha(\mathrm{r}) = \alpha^3\rho(\alpha\mathrm{r})$.

We had proved the identities:

- $\langle\psi_\alpha|T|\psi_\alpha\rangle = \alpha^2\langle\psi|T|\psi\rangle$
- $\langle\psi_\alpha|V(R)|\psi_\alpha\rangle = \alpha\langle\psi|V(\alpha R)|\psi\rangle$

Thomas–Fermi Theory III

Proof of the first result:

$$\begin{aligned}\langle\psi_\alpha|T|\psi_\alpha\rangle &= \alpha^{3N}\int \psi^*(\alpha r_i)\left(-\frac{1}{2}\sum_i \nabla_i^2\right)\psi(\alpha r_i)\prod_i \mathrm{d}r_i \\ &= \int \psi^*(\alpha r_i)\left(-\frac{1}{2}\alpha^2\sum_i \nabla^{\alpha}{}_i^2\right)\psi(\alpha r_i)\prod_i \mathrm{d}(\alpha r_i) \\ &= \alpha^2\int \psi^*(r_i')\left(-\frac{1}{2}\sum_i \nabla'^2_i\right)\psi(r_i')\prod_i \mathrm{d}(r_i') \\ &= \alpha^2\langle\psi|T|\psi\rangle\end{aligned}$$

Thomas–Fermi Theory IV

Q:

Prove the second result, that is:

- $\langle \psi_\alpha | V(R) | \psi_\alpha \rangle = \alpha \langle \psi | V(\alpha R) | \psi \rangle$
- Hence show that for the e-e interaction operator

$$\hat{V}_{\rm ee} = \sum_{i>j} \frac{1}{r_{ij}},$$

we have the scaling relation

$$\langle \psi_\alpha | \hat{V}_{\rm ee} | \psi_\alpha \rangle = \alpha \langle \psi | \hat{V}_{\rm ee} | \psi \rangle$$

Thomas–Fermi Theory V

Anticipating a DFT-terminology we will define

- $T[\Psi] = \langle \Psi | \hat{T} | \Psi \rangle \equiv T[\rho]$
- $V_{\mathrm{ee}}[\Psi] = \langle \Psi | \hat{V}_{\mathrm{ee}} | \Psi \rangle \equiv V_{\mathrm{ee}}[\rho]$

Q: How do we justify terming these functionals of the density?

With this notation, the scaling identities can be written as

- $T[\Psi_\alpha] = \alpha^2 T[\Psi]$
- $V_{\mathrm{ee}}[\Psi_\alpha] = \alpha V_{\mathrm{ee}}[\Psi]$

Alternatively we could write these as functionals of ρ.

Thomas–Fermi Theory VI

Our task now is to derive and expression for $T[\rho]$. To do this we assume that the kinetic energy functional can be written in the form

$$T[\rho] = \int t(\rho) d\mathrm{r}$$

where $t(\rho)$ is a homogeneous function of the density. That is, t is of the form $t(x) = Ax^b$ where b is a real number. Why do we assume this can be done? Well, we could state it as an *ansatz*. But there is another reason why it is possible: it is possible to make this derivation using ideas from the free-electron gas. We won't do this here.

Thomas–Fermi Theory VII

Some important points:

- This ansatz, that $T[\rho]$ is a homogeneous function of ρ is an approximation. It is only ever valid for the free-electron gas.
- Why a homogeneous function? Because if $t(x) = Ax^b$ where b is a real number then we can figure out what b is by scaling x: If $x \rightarrow kx'$ then $t(kx') = A(kx')^b = k^b t(x')$.
- This procedure does not tell us what the coefficient A is.

Thomas–Fermi Theory VIII

Consider the kinetic energy under electronic coordinate scaling:

$$
\begin{aligned}
T[\rho_\alpha] &= \int t(\rho_\alpha(\mathrm{r}))\mathrm{dr} \\
&= \int t(\alpha^3\rho(\alpha\mathrm{r}))\mathrm{dr} \\
&= \alpha^{-3}\int t(\alpha^3\rho(\alpha\mathrm{r}))\mathrm{d}(\alpha\mathrm{r}) \\
&= \alpha^{-3}\int t(\alpha^3\rho(\mathrm{r}))\mathrm{dr}
\end{aligned}
$$

where, in the last step we have made a change of variables. But we also have $T[\rho_\alpha] = \alpha^2 T[\rho]$, therefore

$$
\alpha^{-3}\int t(\alpha^3\rho(\mathrm{r}))\mathrm{dr} = \alpha^2\int \mathrm{t}(\rho(\mathrm{r}))\mathrm{dr}
$$

Thomas–Fermi Theory IX

Therefore

$$t(\alpha^3\rho(\mathrm{r})) = \alpha^5 t(\rho)$$

or, by substituting $\alpha' = \alpha^3$ and then dropping the primes,

$$t(\alpha\rho(\mathrm{r})) = \alpha^{5/3} t(\rho)$$

That is, t is a homogeneous function of degree 5/3 in ρ: $t(\rho) = A\rho^{5/3}$.

Therefore, using $A = C_F$,

$$T[\rho] = C_F \int \rho^{5/3}(\mathrm{r})\mathrm{dr}$$

where it can be shown that $C_F = \frac{3}{10}(3\pi^2)^{2/3} = 2.871\cdots$.

Thomas–Fermi Theory X

What about the functional $V_{\mathrm{ee}}[\rho]$?
It consists of two parts: $V_{\mathrm{ee}}[\rho] = J[\rho] + K[\rho]$. We already know the exact form of the Coulomb part:

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\mathrm{r}_1)\rho(\mathrm{r}_2)}{|\mathrm{r}_1 - \mathrm{r}_2|} d\mathrm{r}_1 \mathrm{d}\mathrm{r}_2$$

The exchange energy functional $K[\rho]$, as part of the full electron–electron energy $V_{\mathrm{ee}}[\rho]$, also involves the operator $1/r$, so the two share the same scaling relation, i.e.,

- $K[\rho_\alpha] = \alpha K[\rho]$

Thomas–Fermi Theory XI

We need to find a density functional for this and we do it the same way as we did the kinetic energy functional: Assume

$$K[\rho] = \int k(\rho(\mathrm{r}))\mathrm{dr}$$

where k is a homogeneous function of ρ and use the scaling relation to find the form of k.

Q: Show that

$$K[\rho] = -C_X \int \rho^{4/3}(\mathrm{r})\mathrm{dr},$$

where it can be shown that the constant $C_X = \frac{3}{4}(\frac{3}{\pi})^{1/3}$. Why is this energy defined to be negative?

Thomas–Fermi Theory XII

Q: Show that the Coulomb energy functional $J[s]$ atisfies the scaling relation:

$$J[\rho_\alpha] = \alpha J[\rho]$$

Thomas–Fermi Theory XIII

Now we define the Thomas–Fermi functional (no exchange in this one):

$$
\begin{aligned}
E_{\mathrm{TF}}[\rho] &= T[\rho] + J[\rho] + \int \rho(\mathrm{r})\mathrm{v}_{\mathrm{ext}}(\mathrm{r})\mathrm{dr} \\
&= C_F \int \rho^{5/3}(\mathrm{r})\mathrm{dr} + \frac{1}{2}\iint \frac{\rho(\mathrm{r}_1)\rho(\mathrm{r}_2)}{|\mathrm{r}_1 - \mathrm{r}_2|}\mathrm{dr}_1\mathrm{dr}_2 + \int \rho(\mathrm{r})\mathrm{v}_{\mathrm{ext}}(\mathrm{r})\mathrm{dr}
\end{aligned}
$$

We minimize $E_{\mathrm{TF}}[\rho]$ subject to the condition $N = \int \rho(\mathrm{r})\mathrm{dr}$ using the Lagrange multiplier μ_{TF}:

$$
\delta\left[E_{\mathrm{TF}}[\rho] - \mu_{\mathrm{TF}}\left(\int \rho(\mathrm{r})\mathrm{dr} - \mathrm{N}\right)\right] = 0
$$

Thomas–Fermi Theory XIV

Q: Show that we get

$$\mu_{\rm TF} = \frac{\delta E_{\rm TF}}{\delta \rho(\mathrm{r})} = \frac{5}{3} C_F \rho^{2/3}(\mathrm{r}) - \phi(\mathrm{r})$$

where $\phi(\mathrm{r}) = \mathrm{v}_{\rm ext}(\mathrm{r}) - \int \frac{\rho(\mathrm{r}')}{|\mathrm{r}-\mathrm{r}'|} d\mathrm{r}'$ is the electrostatic potential.

This can be solved (we will not do it) for atoms, and if you'd like to find out more see Chapters 3 and 6 in "Density functional theory of Atoms and Molecules" by Parr and Yang. The solution to the Thomas–Fermi–Dirac equation is given in Ch. 6.
All Dirac did was to modify the TF functional to include the exchange functional $K[\rho]$. This turned out to result in somewhat worse agreement with the more accurate Hartree–Fock energies.

Thomas–Fermi Theory XV

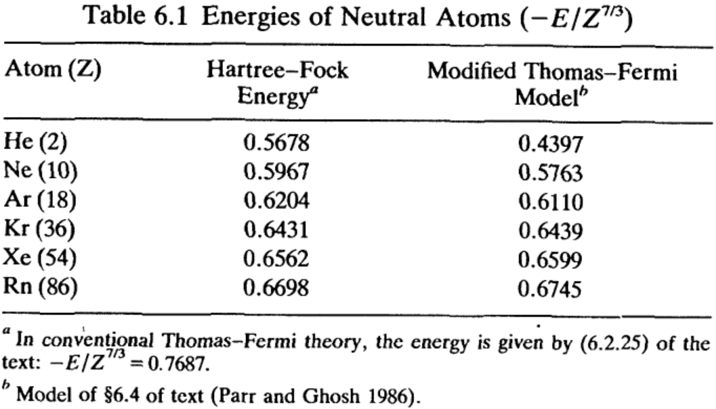


Table 6.1 Energies of Neutral Atoms ($-E/Z^{7/3}$)

Atom (Z)	Hartree–Fock Energy[a]	Modified Thomas–Fermi Model[b]
He (2)	0.5678	0.4397
Ne (10)	0.5967	0.5763
Ar (18)	0.6204	0.6110
Kr (36)	0.6431	0.6439
Xe (54)	0.6562	0.6599
Rn (86)	0.6698	0.6745

[a] In conventional Thomas–Fermi theory, the energy is given by (6.2.25) of the text: $-E/Z^{7/3} = 0.7687$.

[b] Model of §6.4 of text (Parr and Ghosh 1986).

Thomas–Fermi Theory XVI

Another problem with TF/TFD theory is that they do not result in any shell structure. Here's the density of Argon obtained using Hartree–Fock and various modifications of the TFD model:

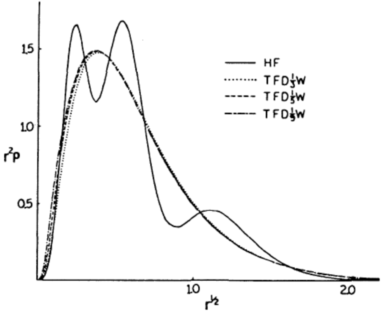


Figure 6.3 Electron density for argon from various models (after Yang 1986.)

Thomas–Fermi Theory XVII

The Thomas–Fermi equations can be solved numerically and a number of trends derived. (As this is an approximate theory, we look for trends rather than quantitative results.) For more about this model, and for a description of extensions that Dirac (and others) made to it, see chapters 3 and 6 in *Density-Functional theory of Atoms and Molecules* by Parr and Yang. These authors are the 'P' and 'Y' in density functionals like BLYP, PBE. The book is meant for Physicists and is quite rigorous. It is an old book (old by the standards of a fast moving field like DFT), so do not expect an exposition of the recent developments, some of which will be discussed in this course.

Functionals I

Revision of functionals and functional derivatives.

See Appendix B in Ullrich's *Time-Dependent Density-Functional Theory* for an overview of this topic. Or else, a mathematical physics book such as the one by Arfken.

Definition of the functional derivative:

$$\boxed{\frac{\delta F[\phi]}{\delta\phi(y)} = \lim_{\epsilon\to 0}\frac{1}{\epsilon}\{F[\phi(x)+\epsilon\delta(x-y)] - F[\phi(x)]\}.}$$

Product Rule:

$$\boxed{\frac{\delta F[\phi]G[\phi]}{\delta\phi(y)} = F[\phi]\frac{\delta G[\phi]}{\delta\phi(y)} + \frac{\delta F[\phi]}{\delta\phi(y)}G[\phi].}$$

Functionals II

Chain Rule:

$$\boxed{\frac{\delta F[\gamma[\phi]]}{\delta\phi(y)} = \int dy' \, \frac{\delta F[\gamma]}{\delta\gamma(y')} \frac{\delta\gamma(y')}{\delta\phi(y)}.}$$

Hartree–Fock again I

Before getting on with DFT, let's have another look at Hartree–Fock, but this time, from a slightly different angle. The HF energy can be written as

$$\begin{aligned} E_{\mathrm{HF}} &= \min_{|\Psi_{\mathrm{SD}}\rangle \to N} \langle \Psi_{\mathrm{SD}} | \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{V}_{\mathrm{ee}} | \Psi_{\mathrm{SD}} \rangle \\ &= \min_{|\Psi_{\mathrm{SD}}\rangle \to N} \langle \Psi_{\mathrm{SD}} | \hat{T} + v_{\mathrm{ext}} + \hat{V}_{\mathrm{ee}} | \Psi_{\mathrm{SD}} \rangle \end{aligned}$$

Here $|\Psi_{\mathrm{SD}}\rangle$ is our Slater determinant that yields an N electron density. In the second line I have used our notation for the electron–nuclear potential: the external potential.

Hartree–Fock again II

This minimization procedure gives rise to an effective Hamiltonian — the Fock operator:

$$f^{\mathrm{HF}}(i) = -\frac{1}{2}\nabla_i^2 - \sum_{\alpha} \frac{Z_\alpha}{r_{i\alpha}} + v^{\mathrm{HF}}(i) \tag{2}$$

The HF potential is an effective potential that contains the effective electron–electron Coulomb and exchange interactions (no correlation!). To get us ready for Kohn–Sham theory, we will make a few changes to the above equation.

Hartree–Fock again III

- First of all recognise that the second term in the Fock operator is just the external potential: v_{ext}
- Next, split the HF operator into its Coulomb and Exchange parts. These are usually labeled by 'J' and 'X', respectively:

$$v^{\mathrm{HF}} = v_{\mathrm{J}} + v_{\mathrm{X}}$$

So our Fock operator is now written as

$$f^{\mathrm{HF}}(i) = -\frac{1}{2}\nabla_i^2 + v_{\mathrm{ext}}(i) + v_{\mathrm{J}}(i) + v_{\mathrm{X}}(i) \tag{3}$$

Hartree–Fock again IV

Now we postulate that the HF ground state energy is a functional of the density and can be written as

$$E_{\mathrm{HF}}[\rho] = T_{\mathrm{S}}[\rho] + J[\rho] + E_{\mathrm{x}}^{\mathrm{HF}}[\rho] + \int \rho(\mathrm{r})\mathrm{v}_{\mathrm{ext}}(\mathrm{r})\mathrm{dr} \tag{4}$$

where the *non-interacting* Kinetic energy functional is

$$T_{\mathrm{S}}[\rho] = -\frac{1}{2}\sum_{i=1}^{N}\langle\chi_i|\nabla^2|\chi_i\rangle \tag{5}$$

Notice that neither $T_{\mathrm{S}}[\rho]$ nor $E_{\mathrm{x}}^{\mathrm{HF}}[\rho]$ are functionals of the density. They depend on the orbitals $\{\chi_i\}$. We will assume that given a density, we can find these orbitals. This is not to be taken for granted, but it is a reasonable assumption that has a (partial) mathematical justification.

Hartree–Fock again V

We have swept some mathematical details under the Physicists rug. In the above, we have assumed that given a density ρ, we can find a set of orbitals $\{\chi_i\}$ that give us the density. It's easy to see how this can be done for 1 and 2-electron systems (can you see it?), but can we assume that it can be done in general? Of course, we can simply assume it can always be done, then proceed with the derivation (as we will do), and see if we come up with a means of making this mapping from ρ to $\{\chi_i\}$ possible, and hence, retrospectively define $T_{\mathrm{S}}[\rho]$ and $E_{\mathrm{x}}^{\mathrm{HF}}[\rho]$ as shown above. This issue is termed the non-interaction *v*-representibility problem and is discussed at length by Parr & Yang.

Hartree–Fock again VI

The Coulomb energy functional is defined as

$$J[\rho] = \frac{1}{2}\iint \frac{\rho(\mathrm{r}_1)\rho(\mathrm{r}_2)}{r_{12}} d\mathrm{r}_1 \mathrm{d}\mathrm{r}_2$$

or we can write this as

$$J[\tilde{\rho}] = \frac{1}{2}\iint \frac{\tilde{\rho}(\mathrm{x}_1)\tilde{\rho}(\mathrm{x}_2)}{r_{12}} \mathrm{d}\mathrm{x}_1 \mathrm{d}\mathrm{x}_2,$$

where $\tilde{\rho}(\mathrm{x}) = \sum_{\mathrm{i}=1}^{\mathrm{N}} \chi_{\mathrm{i}}^{*}(\mathrm{x})\chi_{\mathrm{i}}(\mathrm{x})$ is the density before the spin integration step. That is $\rho(\mathrm{r}) = \int \tilde{\rho}(\mathrm{x})\mathrm{d}\omega$. We will use $\tilde{\rho}$ rather than ρ as it will significantly simplify the functional calculus. In the derivations that follow we will use $\tilde{\rho}(\mathrm{x})$ as the “density”. Once we are done with the derivations, we will switch back to using $\rho(\mathrm{r})$.

Hartree–Fock again VII

The exchange energy functional is non-local and is, like the KE functional, dependent on the HF orbitals:

$$E_{\mathrm{x}}^{\mathrm{HF}}[\tilde{\rho}] = -\frac{1}{2}\sum_{i}^{N}\sum_{j}^{N}\iint \mathrm{dx}_1\mathrm{dx}_2\,\chi_{\mathrm{i}}^{*}(\mathrm{x}_1)\frac{\chi_{\mathrm{j}}^{*}(\mathrm{x}_2)\mathcal{P}_{12}\chi_{\mathrm{j}}(\mathrm{x}_2)}{\mathrm{r}_{12}}\chi_{\mathrm{i}}(\mathrm{x}_1)$$

where $\mathcal{P}_{12}$ is the permutation operator and i and j go over occupied states.

Hartree–Fock again VIII

Looked at in this way HF theory is a kind of density functional theory, but one that is not, even in principle, exact (except for 1-electron systems).

In this formulation of HF theory, we define the HF energy as

$$E^{\mathrm{HF}} = \min_{\tilde{\rho} \to |\Psi_{\mathrm{SD}}\rangle, N} E_{\mathrm{HF}}[\tilde{\rho}]$$

That is, we minimize the functional $E_{\mathrm{HF}}[\tilde{\rho}]$ over all N-electron densities that arise from a Slater determinant. We need to impose the N-electron constraint and this is done using Lagrange multipliers. We minimize the functional:

$$\Omega[\tilde{\rho}] = E_{\mathrm{HF}}[\tilde{\rho}] - \sum_{i,j}^{N} \epsilon_{ij}(\langle \chi_i | \chi_j \rangle - \delta_{ij})$$

Hartree–Fock again IX

Since $\Omega[\tilde{\rho}]$ really is a functional of the orbitals, we need to perform the variation over the orbitals and use the chain rule:

$$\frac{\delta}{\delta \chi_i^*(\mathrm{x})} = \int \mathrm{dx}' \frac{\delta}{\delta \tilde{\rho}(\mathrm{x}')} \frac{\delta \tilde{\rho}(\mathrm{x}')}{\delta \chi_\mathrm{i}^*(\mathrm{x})} \tag{6}$$

Since $\tilde{\rho}(x) = \sum_{i=1}^{N} \chi_i^*(\mathrm{x})\chi_\mathrm{i}(\mathrm{x})$ from the definition of the functional derivative we get:

$$\frac{\delta \tilde{\rho}(\mathrm{x}')}{\delta \chi_i^*(\mathrm{x})} = \chi_i(\mathrm{x})\delta(\mathrm{x} - \mathrm{x}')$$

Hartree–Fock again X

Now consider the functional derivative of $J[\tilde{\rho}]$:

$$
\begin{aligned}
\frac{\delta J[\tilde{\rho}]}{\delta \chi_i^*(\mathrm{x})} &= \int \mathrm{dx}'' \frac{\delta \mathrm{J}[\tilde{\rho}]}{\delta \tilde{\rho}(\mathrm{x}'')} \frac{\delta \tilde{\rho}(\mathrm{x}'')}{\delta \chi_{\mathrm{i}}^*(\mathrm{x})} \\
&= \int \mathrm{dx}'' \frac{\delta}{\delta \tilde{\rho}(\mathrm{x}'')} \left[\frac{1}{2} \iint \frac{\tilde{\rho}(\mathrm{x})\tilde{\rho}(\mathrm{x}')}{|\mathrm{r}-\mathrm{r}'|} \mathrm{dxdx}' \right] \times \chi_{\mathrm{i}}(\mathrm{x}) \delta(\mathrm{r}''-\mathrm{r}) \\
&= \iint \mathrm{dx}''\mathrm{dx}' \frac{\tilde{\rho}(\mathrm{x}')}{|\mathrm{r}''-\mathrm{r}'|} \chi_{\mathrm{i}}(\mathrm{x}) \delta(\mathrm{x}''-\mathrm{x}) \\
&= v_{\mathrm{J}}(\mathrm{r}) \chi_i(\mathrm{x})
\end{aligned}
$$

Do this for all terms and we get back our Fock equation (in a generalised form).

Hartree–Fock again XI

Prove that the variation of

$$\Omega[\tilde{\rho}] = E_{\mathrm{HF}}[\tilde{\rho}] - \sum_{i,j}^{N} \epsilon_{ij}(\langle \chi_i | \chi_j \rangle - \delta_{ij})$$

with respect to χ_i^* does lead to the Fock equations:

Q:

$$f|\chi_i\rangle = \sum_j \epsilon_{ji}|\chi_j\rangle$$

This is the non-canonical form of the Fock equations. As we saw in the Hartree–Fock lectures, with a suitable unitary transformation we can recover the canonical form:

$$f|\chi_i\rangle = \epsilon_i|\chi_i\rangle$$

Kohn–Sham DFT I

From the two Hohenberg–Kohn theorems we know we can write the ground-state energy as a functional of the density:

$$E[\tilde{\rho}] = T[\tilde{\rho}] + V_{\mathrm{ee}}[\tilde{\rho}] + \int v_{\mathrm{ext}}(\mathrm{r})\tilde{\rho}(\mathrm{x})\mathrm{dx}$$

The problem is that we do not know how to define the first two functionals.
We have seen that Thomas–Fermi theory gives us an expression for $T[\rho]$, but we also saw that this expression was too approximate to be of use for atomic/molecular systems as it does not give rise to the shell structure or chemical bonding.

Kohn–Sham DFT II

In 1965 Walter Kohn & Lu Sham put DFT on a practical footing through what is now known as Kohn–Sham DFT. They began by *postulating* the existence of a non-interacting system with external potential $v_{\rm S}$ that yields the *exact density*. That is

$$\mathcal{H}_{\rm KS} = \sum_i \left(-\frac{1}{2}\nabla_i^2 + v_{\rm S}(i) \right)$$

has a ground state single determinant solution with density $\tilde{\rho}$. This is a non-interating system so we can solve it just as we solved the Fock Hamiltonian. The results will be a set of orbitals $\{\chi_i\}$ and orbital eigenvalues $\{\epsilon_i\}$.

Kohn–Sham DFT III

Just as we wrote the kinetic energy in Hartree–Foct, we write the kinetic energy of this Kohn–Sham non-interacting system:

$$T_{\mathrm{S}}[\tilde{\rho}] = \sum_{i}^{N} -\frac{1}{2}\langle\chi_i|\nabla^2|\chi_i\rangle$$

What Kohn & Sham did was to state that this non-interacting kinetic energy functional $T_{\mathrm{S}}[\tilde{\rho}]$ could be considered a good approximation to the true functional $T[\tilde{\rho}]$.
Importantly, they knew (from Hartree–Fock theory) that $T_{\mathrm{S}}[\tilde{\rho}]$, as it depended on the orbitals, could describe the molecular shell structure.

Kohn–Sham DFT IV

Using $T_{\rm S}[\tilde{\rho}]$, we can write the Hohenberg–Kohn functional as

$$\begin{aligned} F[\tilde{\rho}] &= T[\tilde{\rho}] + V_{\rm ee}[\tilde{\rho}] \\ &= T_{\rm S}[\tilde{\rho}] + J[\tilde{\rho}] + E_{\rm xc}[\tilde{\rho}] \end{aligned}$$

where this eXchange-Correlation functional is defined as

$$E_{\rm xc}[\tilde{\rho}] = (T[\tilde{\rho}] - T_{\rm S}[\tilde{\rho}]) - (V_{\rm ee}[\tilde{\rho}] - J[\tilde{\rho}])$$

The idea here is that we have defined as much as we could define ($T_{\rm S}[\tilde{\rho}]$ and $J[\tilde{\rho}]$), and have swept the rest of the energy into the unknown functional $E_{\rm xc}[\tilde{\rho}]$.

Kohn–Sham DFT V

So we get the following functional for the ground state energy:

$$E[\tilde{\rho}] = T_{\mathrm{S}}[\tilde{\rho}] + J[\tilde{\rho}] + E_{\mathrm{xc}}[\tilde{\rho}] + \int v_{\mathrm{ext}}(\mathrm{r})\tilde{\rho}(\mathrm{x})\mathrm{dx} \tag{7}$$

Compare this to what we had for the Hartree–Fock functional:

$$E_{\mathrm{HF}}[\tilde{\rho}] = T_{\mathrm{S}}[\tilde{\rho}] + J[\tilde{\rho}] + E_{\mathrm{x}}^{\mathrm{HF}}[\tilde{\rho}] + \int \tilde{\rho}(\mathrm{x})\mathrm{v}_{\mathrm{ext}}(\mathrm{r})\mathrm{dx}$$

The difference between the two is that $E_{\mathrm{HF}}[\tilde{\rho}]$ is necessarily approximate while $E[\tilde{\rho}]$ is exact, albeit, *in principal*.

Kohn–Sham DFT VI

$$\boxed{E[\tilde{\rho}] = T_{\mathrm{S}}[\tilde{\rho}] + J[\tilde{\rho}] + E_{\mathrm{xc}}[\tilde{\rho}] + \int v_{\mathrm{ext}}(\mathrm{r})\tilde{\rho}(\mathrm{x})\mathrm{dx} \qquad (8)}$$

must be minimized subject to the orthonormality constraints

$$\langle \chi_i | \chi_j \rangle = \delta_{ij}.$$

As before, we include these constraints using Lagrange multipliers and minimize

$$\Omega[\tilde{\rho}] = E[\tilde{\rho}] - \sum_{i,j}^{N} \epsilon_{ij}(\langle \chi_i | \chi_j \rangle - \delta_{ij})$$

Kohn–Sham DFT VII

This gives us the Kohn–Sham equations after the usual occupied orbital rotation to make the eigenvalue matrix ϵ_{ij} diagonal:

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{S}}(\mathrm{r})\right)\chi_i = \epsilon_i\chi_i$$

where the effective potential is defined as

$$v_{\mathrm{S}}(\mathrm{r}) = \mathrm{v_J}(\mathrm{r}) + \mathrm{v_{ext}}(\mathrm{r}) + \mathrm{v_{xc}}(\mathrm{r})$$

Kohn–Sham DFT VIII

The various potentials that enter this expression are:

- v_{J}: The Coulomb potential defined as:

$$v_{\mathrm{J}}(\mathrm{r}) = \int \frac{\tilde{\rho}(\mathrm{x}')}{|\mathrm{r} - \mathrm{r}'|} \mathrm{dx}' = \int \frac{\rho(\mathrm{r}')}{|\mathrm{r} - \mathrm{r}'|} \mathrm{dr}'$$

- v_{ext}: The external potential, i.e., the electron-nuclear potential:

$$v_{\mathrm{ext}}(\mathrm{r}) = -\sum_{\alpha} \frac{\mathrm{Z}_{\alpha}}{|\mathrm{r} - \mathrm{R}_{\alpha}|}$$

Kohn–Sham DFT IX

- $v_{\rm xc}$: The exchange-correlation potential which is defined through the exchange-correlation energy $E_{\rm xc}[\tilde{\rho}]$ as:

$$v_{\rm xc}(\rm r) \equiv \rm v_{\rm xc}(\rm x) = \frac{\delta \rm E_{\rm xc}[\tilde{\rho}]}{\delta \tilde{\rho}(\rm x)}$$

  As will be explained below, $v_{\rm xc}$ will be spin-independent for us, so we can make this equivalence.

Let's see how these potentials arise.

Kohn–Sham DFT X

Once again, since $\Omega[\tilde{\rho}]$ really is a functional of the orbitals, we need to perform the variation over the orbitals and use the chain rule:

$$\frac{\delta}{\delta\chi_i^*(\mathrm{x})} = \int d\mathrm{x}' \frac{\delta}{\delta\tilde{\rho}(\mathrm{x}')}\frac{\delta\tilde{\rho}(\mathrm{x}')}{\delta\chi_\mathrm{i}^*(\mathrm{x})} \qquad (9)$$

For a single determinant wavefunction $\tilde{\rho}(\mathrm{x}) = \sum_{\mathrm{i}=1}^{\mathrm{N}} \chi_\mathrm{i}^*(\mathrm{x})\chi_\mathrm{i}(\mathrm{x})$, so we get

$$\frac{\delta\tilde{\rho}(\mathrm{x}')}{\delta\chi_i^*(\mathrm{x})} = \chi_i(\mathrm{x})\delta(\mathrm{x}' - \mathrm{x})$$

More generally, for a multi-determinant wavefunction

$$\tilde{\rho}(\mathrm{x}) = \sum_{i=1}^{N_{\mathrm{basis}}} f_i\chi_i^*(\mathrm{x})\chi_\mathrm{i}(\mathrm{x}),$$

where N_{basis} is the size of the basis, i.e., the size of the function space we are working in. Here the f_i are occupation numbers that satisfy $0 \leq f_i \leq 1, \forall i$ and $\sum_i f_i = N$, where N is the number of electrons.

Kohn–Sham DFT XI

We have already shown that the functional derivative of $J[\tilde{\rho}]$ is:

$$\frac{\delta J[\tilde{\rho}]}{\delta \chi_i^*(\mathrm{x})} = v_{\mathrm{J}}(\mathrm{r})\chi_i(\mathrm{x}),$$

but let's see this again:

$$\begin{aligned}
\frac{\delta J[\tilde{\rho}]}{\delta \chi_i^*(\mathrm{x})} &= \int d\mathrm{x}''' \frac{\delta \mathrm{J}[\tilde{\rho}]}{\delta \tilde{\rho}(\mathrm{x}''')} \frac{\delta \tilde{\rho}(\mathrm{x}''')}{\delta \chi_{\mathrm{i}}^*(\mathrm{x})} \\
&= \int d\mathrm{x}''' \frac{\delta}{\delta \tilde{\rho}(\mathrm{x}''')} \left[\frac{1}{2} \iint \frac{\tilde{\rho}(\mathrm{x}')\tilde{\rho}(\mathrm{x}'')}{|\mathrm{r}' - \mathrm{r}''|} \mathrm{dx}'\mathrm{dx}'' \right] \times \chi_{\mathrm{i}}(\mathrm{x})\delta(\mathrm{x}''' - \mathrm{x}) \\
&= \iint d\mathrm{x}'''\mathrm{dx}' \frac{\tilde{\rho}(\mathrm{x}')}{|\mathrm{r}''' - \mathrm{r}'|} \chi_{\mathrm{i}}(\mathrm{x})\delta(\mathrm{x}''' - \mathrm{x}) \\
&= \left(\int \mathrm{dx}' \frac{\tilde{\rho}(\mathrm{x}')}{|\mathrm{r} - \mathrm{r}'|} \right) \chi_i(\mathrm{x}) = \mathrm{v}_{\mathrm{J}}(\mathrm{r})\chi_{\mathrm{i}}(\mathrm{x})
\end{aligned}$$

Kohn–Sham DFT XII

Now consider the functional derivative of $E_{\mathrm{ext}}[\tilde{\rho}] = \int v_{\mathrm{ext}}(\mathrm{r})\tilde{\rho}(\mathrm{x})\mathrm{dx}$:

$$\begin{aligned}\frac{\delta E_{\mathrm{ext}}[\tilde{\rho}]}{\delta \chi_i^*(\mathrm{x})} &= \int \mathrm{dx}' \frac{\delta \mathrm{E}_{\mathrm{ext}}[\tilde{\rho}]}{\delta \tilde{\rho}(\mathrm{x}')} \frac{\delta \tilde{\rho}(\mathrm{x}')}{\delta \chi_{\mathrm{i}}^*(\mathrm{x})} \\ &= \int \mathrm{dx}' \mathrm{v}_{\mathrm{ext}}(\mathrm{r}') \times \chi_{\mathrm{i}}(\mathrm{x})\delta(\mathrm{x}' - \mathrm{x}) \\ &= v_{\mathrm{ext}}(\mathrm{r})\chi_i(\mathrm{x})\end{aligned}$$

We cannot evaluate the functional derivative of $E_{\mathrm{xc}}[\tilde{\rho}]$ as we still do not know the form of this functional. So we simply define:

$$v_{\mathrm{xc}}(\mathrm{r}) \equiv \mathrm{v}_{\mathrm{xc}}(\mathrm{x}) = \frac{\delta \mathrm{E}_{\mathrm{xc}}[\tilde{\rho}]}{\delta \tilde{\rho}(\mathrm{x})}$$

We can state that $v_{\mathrm{xc}}(\mathrm{r}) \equiv \mathrm{v}_{\mathrm{xc}}(\mathrm{x})$ as v_{xc} will be spin-independent as far as we are concerned.

Kohn–Sham DFT XIII

So the Kohn–Sham non-interacting potential is defined as:

$$\boxed{\begin{aligned} v_{\mathrm{S}}(\mathrm{r}) &= v_{\mathrm{J}}(\mathrm{r}) + \mathrm{v}_{\mathrm{ext}}(\mathrm{r}) + \mathrm{v}_{\mathrm{xc}}(\mathrm{r}) \\ &= \int \frac{\tilde{\rho}(\mathrm{x}')}{|\mathrm{r}-\mathrm{r}'|}\mathrm{dx}' + \mathrm{v}_{\mathrm{ext}}(\mathrm{r}) + \frac{\delta \mathrm{E}_{\mathrm{xc}}[\tilde{\rho}]}{\delta \tilde{\rho}(\mathrm{x})} \end{aligned}}$$

We solve the 1-electron Kohn–Sham equations self-consistently:

$$\boxed{k(1)\chi_i(1) = \left(-\frac{1}{2}\nabla_1^2 + v_{\mathrm{S}}(1)\right)\chi_i(1) = \epsilon_i \chi_i(1)}$$

where we have defined the Kohn–Sham operator $k(1)$.

Kohn–Sham DFT XIV

Once we have the orbitals χ_i, we can evaluate the energy using

$$\boxed{E[\tilde{\rho}] = T_{\mathrm{S}}[\tilde{\rho}] + J[\tilde{\rho}] + E_{\mathrm{xc}}[\tilde{\rho}] + \int v_{\mathrm{ext}}(\mathrm{r})\tilde{\rho}(\mathrm{x})\mathrm{dx}}$$

NOTE: Now that we are done with the derivation, we move back to using $\rho(\mathrm{r})$ instead of $\tilde{\rho}(\mathrm{x})$.
Recall that $\rho(\mathrm{r}) = \int \tilde{\rho}(\mathrm{x})\mathrm{d}\sigma$. So the above can be written as:

$$\boxed{E[\rho] = T_{\mathrm{S}}[\rho] + J[\rho] + E_{\mathrm{xc}}[\rho] + \int v_{\mathrm{ext}}(\mathrm{r})\rho(\mathrm{r})\mathrm{dr}}$$

Kohn–Sham DFT XV

Equivalently, we may use the results derived when studying Hartree–Fock to relate energy to the orbital energies:

$$\begin{aligned}
\sum_i \epsilon_i &= \langle \Psi_0 | \sum_i k(i) | \Psi_0 \rangle \\
&= \langle \Psi_0 | \sum_i \left(-\frac{1}{2} \nabla_i^2 + v_{\mathrm{S}}(i) \right) | \Psi_0 \rangle \\
&= \langle \Psi_0 | \sum_i -\frac{1}{2} \nabla_i^2 | \Psi_0 \rangle + \langle \Psi_0 | \sum_i v_{\mathrm{S}}(i) | \Psi_0 \rangle \\
&= T_{\mathrm{S}}[\rho] + \langle \Psi_0 | \sum_i \left(v_{\mathrm{J}}(i) + v_{\mathrm{ext}}(i) + v_{\mathrm{xc}}(i) \right) | \Psi_0 \rangle \\
&= T_{\mathrm{S}}[\rho] + 2J[\rho] + \int v_{\mathrm{ext}}(\mathrm{r}) \rho(\mathrm{r}) \mathrm{dr} + \int \mathrm{v}_{\mathrm{xc}}(\mathrm{r}) \rho(\mathrm{r}) \mathrm{dr}
\end{aligned}$$

Kohn–Sham DFT XVI

Using this, we can write an expression for the kinetic energy functional:

$$T_{\mathrm{S}}[\rho] = \sum_i \epsilon_i - 2J[\rho] - \int v_{\mathrm{ext}}(\mathrm{r})\rho(\mathrm{r})\mathrm{dr} - \int \mathrm{v}_{\mathrm{xc}}(\mathrm{r})\rho(\mathrm{r})\mathrm{dr}$$

And then we can write the total energy:

$$\begin{aligned} E[\rho] &= T_{\mathrm{S}}[\rho] + J[\rho] + E_{\mathrm{xc}}[\rho] + \int v_{\mathrm{ext}}(\mathrm{r})\rho(\mathrm{r})\mathrm{dr} \\ &= \sum_i \epsilon_i - J[\rho] + E_{\mathrm{xc}}[\rho] - \int v_{\mathrm{xc}}(\mathrm{r})\rho(\mathrm{r})\mathrm{dr} \end{aligned}$$

Kohn–Sham DFT XVII

- In a sense, what Kohn & Sham did was to sweep all the unknowns under the rug. But they did this intelligently as they had a good idea of how to approximate the unknown bits: the exchange-correlation energy and its functional derivative.
- Also, they knew that their formalism was *in principle* exact as they had proved various theorems to that effect.
- It turned out that their proofs were not mathematically sound, but this was fixed by others.
- The rest of the DFT story is how we find the exchange-correlation functional $E_{\rm xc}[\rho]$.

Kohn–Sham DFT XVIII

Q: Use the Slater–Condon rules for integrals to show the last step in the previous equation. We have already shown that, for a one-electron spin-free operator $\hat{v}$ we have

$$\langle \Psi | v | \Psi \rangle = \int \rho(\mathrm{r}) \mathrm{v}(\mathrm{r}) \mathrm{dr}.$$

Start from there (or elsewhere if you prefer) and show the previous result.

Why do we get a 2 in front of the Coulomb functional? Make sure you see how this arises.

Density Functionals I

Exchange correlation functionals are usually written in the form

$$E_{\rm xc}[\rho] = \int \rho({\rm r})\epsilon_{\rm xc}(\rho({\rm r}), \nabla\rho({\rm r}), \cdots){\rm dr} \tag{10}$$

where $\epsilon_{\rm xc}(\rho({\rm r}), \nabla\rho({\rm r}), \cdots)$ can be regarded as the exchange-correlation density.

We usually split the exchange-correlation density into its exchange and correlation parts:

$$\epsilon_{\rm xc}(\rho({\rm r}), \nabla\rho({\rm r}), \cdots) = \epsilon_{\rm x}(\rho({\rm r}), \nabla\rho({\rm r}), \cdots) + \epsilon_{\rm c}(\rho({\rm r}), \nabla\rho({\rm r}), \cdots) \tag{11}$$

This separation is convenient for we can then think of using well-understood approximations for each of these.

LDA I

The first of the many functionals is the local density approximation or LDA. In this approximation the exchange-correlation density depends on the electron density alone (no dependence on gradients etc.):

$$E_{\mathrm{xc}}[\rho] = \int \rho(\mathrm{r})\epsilon_{\mathrm{xc}}^{\mathrm{LDA}}(\rho(\mathrm{r}))\mathrm{dr} \tag{12}$$

The Slater approximation is used for the exchange-energy density:

$$\epsilon_{\mathrm{x}}^{\mathrm{S}}(\rho(\mathrm{r})) = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{3/2}\rho^{1/3}(\mathrm{r})$$

Using this we get the Slater exchange functional:

$$E_{\mathrm{x}}^{\mathrm{S}}[\rho] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{3/2}\int \rho^{4/3}(\mathrm{r})\mathrm{dr} = -\mathrm{C_x}\int \rho^{4/3}(\mathrm{r})\mathrm{dr}$$

LDA II

Paired with this is a correlation functional parameterized on very accurate quantum Monte-Carlo (QMC) calculations of the energy of the homogeneous free electron gas as a function of density. There are a variety of correlation parameterizations. These differ by the choice of QMC energies used or by the interpolation scheme used in the parameterization (the QMC energies are calculated at a set of densities so some scheme is required to interpolate to all densities).

Common choices of the correlation functional are:

- PW91c The Perdew–Wang (1992) parameterization (called `pw91lda` in NWCHEM.
- VWN The Vosko–Wilk–Nusair (1980) parameterization.

So what is called the LDA translates into a combination of the Slater exchange functional and one of these correlation functionals. The actual choice will vary with program.

LDA III

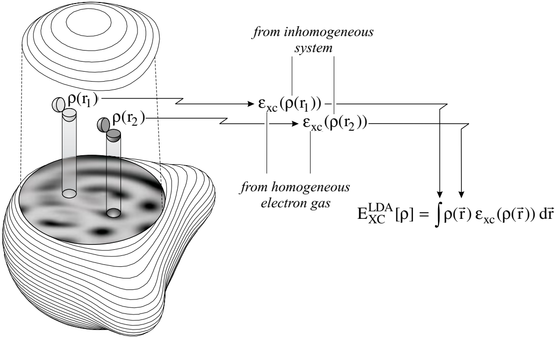


Figure 6-2. The local density approximation.

From Koch & Holthausen *A Chemist's Guide to density Functional Theory* (2001).

LDA IV

Generalization to open-shell systems (local spin-density approximation (LSD)): the exchange-correlation density depends on the spin-up and spin-down densities:

$$E_{\mathrm{xc}}[\rho_\alpha, \rho_\beta] = \int \rho(\mathrm{r})\epsilon_{\mathrm{xc}}^{\mathrm{LDA}}(\rho_\alpha(\mathrm{r}), \rho_\beta(\mathrm{r}))\mathrm{d}\mathrm{r} \qquad (13)$$

- GOOD LDA is better than HF. Good equilibrium geometries, harmonic frequencies.
- BAD Energetics very poor. Errors in atomization energies 36 kcal/mol. (HF has errors of 78 kcal/mol on same set of molecules)

GGA I

In the generalized gradient approximations the exchange-correlation density is dependent on the density and its gradient.

$$E_{\mathrm{xc}}[\rho] = \int \rho(\mathrm{r})\epsilon_{\mathrm{xc}}^{\mathrm{GGA}}(\rho(\mathrm{r}), \nabla\rho(\mathrm{r}))\mathrm{dr}$$

As before, we split the exchange-correlation density into its exchange and correlation parts:

$$\epsilon_{\mathrm{xc}}^{\mathrm{GGA}}(\rho(\mathrm{r}), \nabla\rho(\mathrm{r})) = \epsilon_{\mathrm{x}}^{\mathrm{GGA}}(\rho(\mathrm{r}), \nabla\rho(\mathrm{r})) + \epsilon_{\mathrm{c}}^{\mathrm{GGA}}(\rho(\mathrm{r}), \nabla\rho(\mathrm{r}))$$

The exchange part of all GGAs takes the form

$$E_{\mathrm{x}}^{\mathrm{GGA}}[\rho] = \int \rho(\mathrm{r})\epsilon_{\mathrm{x}}^{\mathrm{LDA}}(\rho(\mathrm{r}))\mathrm{F}_{\mathrm{x}}(\mathrm{s})\mathrm{dr}$$

GGA II

$F_{\mathrm{x}}(s)$ is called the enhancement factor and is written as a function of the reduced density gradient defined as

$$s(\mathrm{r}) = \frac{|\nabla\rho(\mathrm{r})|}{2(3\pi^2)^{1/3}\rho^{4/3}(\mathrm{r})}.$$

Note that in general all quantities will depend on spin.

Q: Show that the reduced density gradient s is dimensionless.

This is important as mathematical expansions of physical quantities are best done in terms of a dimensionless quantity. Imagine how we could make a power series in terms of a variable x having the units of length. Much better to use x/x_0, where x_0 is some characteristic length, as this ratio is dimensionless.

GGA III

But there is another reason for choosing to use the reduced density gradient: As s is large both when the gradient of the density is large (where the LDA should fail) and also where the density is small (in the region of the density tails, where once again, LDA should be a poor approximation), it is natural to expand the correction in terms of this variable as it picks out exactly those places where a correction is required.

GGA IV

Two of the common exchange enhancement factors are

- Becke, 1988 (B88)

$$F_{\mathrm{x}}^{\mathrm{B88}}(s) = 1 - \frac{\beta s^2}{1 + 6\beta s \sinh^{-1} s}$$

  Becke fitted the parameter $\beta = 0.0042$ to reproduce known exchange energies of rare gas atoms. This particular form for the enhancement factor was chosen to obey a few exact relations.

- Perdew, Burke & Ernzerhof, 1996 (PBE)

$$F_{\mathrm{x}}^{\mathrm{PBE}}(s) = 1 + \kappa - \frac{\kappa}{1 - \mu s^2/\kappa}$$

  In this functional all parameters were obtained theoretically. $\kappa = 0.804$. Most physcists use this exchange functional.

Hybrid Functionals I

The exchange contribution to the energy is much larger than the correlation energy (which is why HF is not too bad!). So why not use the best exchange energy we have — from HF, usually termed *exact* exchange in this context — and combine it with the best correlation funtional available:

$$E_{\mathrm{xc}}[\rho] = E_{\mathrm{x}}^{\mathrm{HF}}[\rho] + E_{\mathrm{c}}[\rho]$$

This turns out to be better than HF, but much worse than the GGAs.

This has to do with a cancellation of errors that occurs when we pair a local exchange functional with a local correlation functional, but does not happen when the latter is paired with the non-local HF-type exchange functional.

Hybrid Functionals II

In 1993, Becke proposed a three-parameter semi-empirical functional that cured this problem. The general idea is to mix some fraction of HF exchange with DFT exchange:

$$E_{\mathrm{xc}}^{\mathrm{hybrid}} = aE_{\mathrm{x}}^{\mathrm{HF}} + (1-a)E_{\mathrm{x}}^{\mathrm{GGA}} + E_{\mathrm{c}}^{\mathrm{GGA}}$$

The B3LYP is the most widely used of these and is a slight modification of Becke's 1993 proposal made the following year by Stephens and others:

$$\begin{aligned} E_{\mathrm{xc}}^{\mathrm{B3LYP}} =& E_{\mathrm{xc}}^{\mathrm{SVWN}} + a_0(E_{\mathrm{x}}^{\mathrm{HF}} - E_{\mathrm{x}}^{\mathrm{S}}) + a_x(E_{\mathrm{x}}^{\mathrm{B88}} - E_{\mathrm{x}}^{\mathrm{S}}) \\ &+ a_c(E_{\mathrm{c}}^{\mathrm{LYP}} - E_{\mathrm{c}}^{\mathrm{VWN}}) \end{aligned}$$

A better choice (in my opinion) is the PBE0 functional (sometimes called PBE1PBE) which mixes PBE with 25% HF exchange.

Hybrid Functionals III

In a sense, hybrid functional are simply linear combinations of the Kohn–Sham and Hartree–Fock energy functionals:

$$E[\rho] = T_{\mathrm{S}}[\rho] + J[\rho] + \color{blue}{E_{\mathrm{xc}}[\rho]} + \int v_{\mathrm{ext}}(\mathrm{r})\rho(\mathrm{r})\mathrm{dr}$$

and

$$E_{\mathrm{HF}}[\rho] = T_{\mathrm{S}}[\rho] + J[\rho] + \color{red}{E_{\mathrm{x}}^{\mathrm{HF}}[\rho]} + \int v_{\mathrm{ext}}(\mathrm{r})\rho(\mathrm{r})\mathrm{dr}$$

Functionally, all terms, but those in colour, are the same. So if we take a linear-combination of the two we get the hybrid functionals.

$$\begin{aligned} E^{\mathrm{hyb}}[\rho] &= (1-x)\ E[\rho] + (x)\ E_{\mathrm{HF}}[\rho] \\ &= T_{\mathrm{S}}[\rho] + J[\rho] + (1-x)\color{blue}{E_{\mathrm{xc}}[\rho]} + (x)\color{red}{E_{\mathrm{x}}^{\mathrm{HF}}[\rho]} + \int v_{\mathrm{ext}}(\mathrm{r})\rho(\mathrm{r})\mathrm{dr}. \end{aligned}$$

Other types of linear combinations are possible and these lead to the range-separated functionals.

Jacob’s Ladder I

John Perdew has summarised the state of DFT using the Biblical picture of Jacob’s Ladder: At the base we have the LDA and at the top, in the heaven of chemical accuracy (interesting concept - what is Physical Accuracy?) we have some unknown functional. Here’s the whole Ladder...

Jacob's Ladder II

CHEMICAL HEAVEN

1. corr-hyper-GGA: Modifies the hyper-GGAs by including correlation through range-separation. This is currently done at the RPA level.
2. hyper-GGA: Adds exact exchange using range-separation. Leads to functionals that can fix (part of) the charge-transfer problem of most DFT functionals. CamB3LYP
3. meta-GGA: $\rho, \nabla\rho, \nabla^2\rho, \tau$, here $\tau = \frac{1}{2}\sum_{a\in\mathrm{occ}} |\nabla\chi_a|^2$ is the Kohn–Sham orbital kinetic energy density. TPSS
4. GGA: $\rho, \nabla\rho$. PBE
5. LDA,LSD: ρ

INACCURATE HELL

Jacob's Ladder III

A philosophical question:
Is Kohn–Sham theory a density-functional theory?

Thomas–Fermi theory is definitely a density-functional theory. But in Kohn–Sham theory we work with the spin orbitals and use these to define the kinetic energy functional, and also, in hybrid functionals, the exchange functional.
Perhaps we should refer to this theory not as *density functional theory*, but as *Kohn–Sham theory*. Some authors do make this distinction and call modern 'density-functional theory' as KS-DFT. This is good practice.