

Ab initio methods: The e-e cusp and DFT

Alston J. Misquitta

Centre for Condensed Matter and Materials Physics
Queen Mary, University of London

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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 (MP n)**: 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

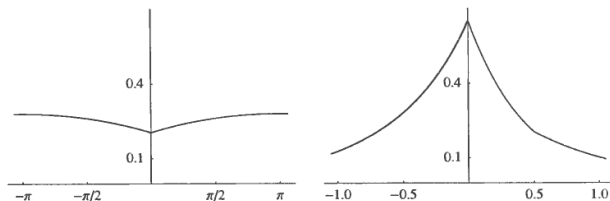


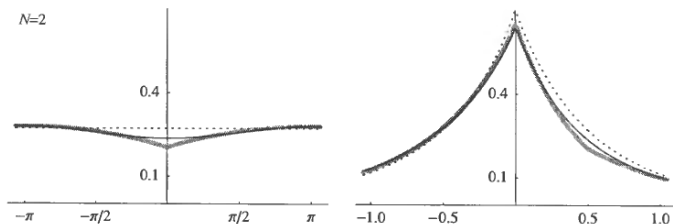
Fig. 7.5. The electronic and nuclear cusps of the ground-state helium atom with one electron fixed at a position $0.5a_0$ from the nucleus (atomic units). On the left, the wave function is plotted on a circle of radius $0.5a_0$ centred at the nucleus; on the right, the wave function is plotted along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

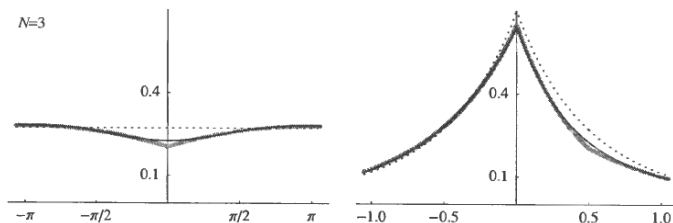
The electron–electron cusp III

He₂: Principle wave expansion with one electron fixed at 0.5Å:
 $n = 2$



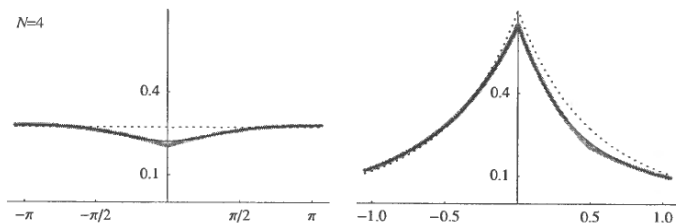
The electron–electron cusp IV

He₂: Principle wave expansion with one electron fixed at 0.5Å:
 $n = 3$



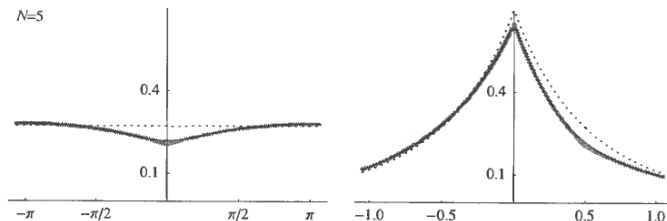
The electron–electron cusp V

He₂: Principle wave expansion with one electron fixed at 0.5Å:
 $n = 4$



The electron–electron cusp VI

He₂: 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:

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

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):

$$\mathcal{H} = -\frac{1}{2} \sum_i^N \nabla_i^2 + \sum_{i<j} \frac{1}{r_{ij}} + \sum_i^N v_{\text{ext}}(\mathbf{r}_i) \quad (1)$$

- 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

$$\begin{aligned}
 E_1^0 &< \langle \Psi_2 | \mathcal{H}_1 | \Psi_2 \rangle = \langle \Psi_2 | \mathcal{H}_2 | \Psi_2 \rangle + \langle \Psi_2 | \mathcal{H}_1 - \mathcal{H}_2 | \Psi_2 \rangle \\
 &= E_2^0 + \langle \Psi_2 | v_{\text{ext}}^1 - v_{\text{ext}}^2 | \Psi_2 \rangle \\
 &= E_2^0 + \int \rho(\mathbf{r}) [v_{\text{ext}}^1(\mathbf{r}) - v_{\text{ext}}^2(\mathbf{r})] d\mathbf{r}
 \end{aligned}$$

- Similarly $E_2^0 < E_1^0 + \int \rho(\mathbf{r}) [v_{\text{ext}}^2(\mathbf{r}) - v_{\text{ext}}^1(\mathbf{r})] d\mathbf{r}$
- Adding the inequalities:

$$E_1^0 + E_2^0 < E_2^0 + E_1^0 \quad \rightarrow \leftarrow$$

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

Density-Functional Theory IV

E. 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:

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

$$\left. \frac{\partial}{\partial r} \langle \rho(r) \rangle_{\text{sph}} \right|_{r=0} = -2Z \langle \rho(0) \rangle_{\text{sph}}$$

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

Density-Functional Theory V

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

$$\begin{aligned} E &= E[\rho] = T[\rho] + V_{ee}[\rho] + V_{en}[\rho] \\ &= F[\rho] + \int \rho(\mathbf{r})v_{\text{ext}}(\mathbf{r})d\mathbf{r} \end{aligned}$$

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 VI

It's easy to see how this theorem arises:

- $\tilde{\rho}$ gives rise to a unique potential $v_{\text{ext}}^{\tilde{\rho}}$, and hence a Hamiltonian $\tilde{\mathcal{H}}$ and therefore to a ground state wavefunction $\tilde{\Psi}$.
- Using the variational principle

$$E^0 = E[\rho] \leq \langle \tilde{\Psi} | \mathcal{H} | \tilde{\Psi} \rangle = F[\tilde{\rho}] + \int \tilde{\rho}(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r} = E[\tilde{\rho}]$$

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

Density-Functional Theory VII

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 $v_{\text{ext}}^{\tilde{\rho}}$? 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.

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

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

Here $|\Psi_{\text{SD}}\rangle$ 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:

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

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:

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

So our Fock operator is now written as

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

Hartree–Fock again IV

In some sense we can say that the HF ground state energy is a functional of the density and can be written as

$$E_{\text{HF}}[\rho^{\text{HF}}] = T_{\text{S}}[\rho^{\text{HF}}] + J[\rho^{\text{HF}}] + E_{\text{x}}^{\text{HF}}[\rho^{\text{HF}}] + \int \rho^{\text{HF}}(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r} \quad (4)$$

where the *non-interacting* Kinetic energy functional is

$$T_{\text{S}}[\rho^{\text{HF}}] = -\frac{1}{2} \sum_{i=1}^N \langle \chi_i | \nabla_i^2 | \chi_i \rangle \quad (5)$$

which is not strictly a functional of the density, but since the density is implicitly a functional of the orbitals we can still think of the KE functional as a density functional.

Hartree–Fock again V

The Coulomb energy functional is defined as

$$J[\rho^{\text{HF}}] = \frac{1}{2} \iint \frac{\rho^{\text{HF}}(\mathbf{r}_1)\rho^{\text{HF}}(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \quad (6)$$

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

$$E_x^{\text{HF}}[\rho^{\text{HF}}] = - \sum_{a \in \text{occ}} \sum_{b \in \text{occ}} \iint d\mathbf{x}_1 d\mathbf{x}_2 \chi_a^*(1) \frac{\chi_b^*(2) \mathcal{P}_{12} \chi_b(2)}{r_{12}} \chi_a(1) \quad (7)$$

where \mathcal{P}_{12} is the permutation operator.

Hartree–Fock again VI

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

$$E^{\text{HF}} = \min_{\rho \rightarrow |\Psi_{\text{SD}}\rangle, N} E_{\text{HF}}[\rho]$$

That is, we minimize the functional $E_{\text{HF}}[\rho]$ 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:

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

Hartree–Fock again VII

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

$$\frac{\delta}{\delta\chi_i(\mathbf{r})} = \frac{\delta}{\delta\rho(\mathbf{r})} \frac{\delta\rho(\mathbf{r})}{\delta\chi_i(\mathbf{r})} \quad (8)$$

I do not want to get bogged down with functional derivatives, but one example of how its done could be illuminating:

First of all, since $\rho(\mathbf{r}) = \sum_{i=1}^N \chi_i^*(\mathbf{r})\chi_i(\mathbf{r})$ we get

$$\frac{\delta\rho(\mathbf{r})}{\delta\chi_i^*(\mathbf{r})} = \chi_i(\mathbf{r})$$

Hartree–Fock again VIII

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

$$\begin{aligned}\frac{\delta J[\rho]}{\delta \chi_i^*(\mathbf{r})} &= \frac{\delta J[\rho]}{\delta \rho(\mathbf{r})} \frac{\delta \rho(\mathbf{r})}{\delta \chi_i^*(\mathbf{r})} \\ &= \frac{\delta}{\delta \rho(\mathbf{r})} \left[\frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \right] \times \chi_i(\mathbf{r}) \\ &= \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \chi_i(\mathbf{r}) \\ &= v_J(\mathbf{r})\chi_i(\mathbf{r})\end{aligned}$$

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

Kohn–Sham DFT I

Now we are in a position to appreciate Kohn–Sham DFT. They began by *postulating* the existence of a non-interacting system with external potential v_S that yields the *exact density*. That is

$$\mathcal{H} = \sum_i \left(-\frac{1}{2} \nabla_i^2 + v_S(i) \right)$$

has a ground state single determinant solution with density ρ .

Kohn–Sham DFT II

We know how to write the kinetic energy of this system:

$$T_S[\rho] = \sum_i^N -\frac{1}{2} \langle \chi_i | \nabla^2 | \chi_i \rangle$$

Now write the Hohenberg–Kohn functional as

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

where this eXchange-Correlation functional is defined as

$$E_{xc}[\rho] = (T[\rho] - T_S[\rho]) - (V_{ee}[\rho] - J[\rho])$$

Kohn–Sham DFT III

To find out what goes into this mysterious effective potential v_S we write down the Kohn–Sham energy functional:

$$E[\rho] = T_S[\rho] + J[\rho] + E_{xc}[\rho] + \int v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \quad (9)$$

As with our Hartree–Fock functional, this needs to be minimized subject to the constraints

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

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

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

Kohn–Sham DFT IV

which after a little manipulation gives us the Kohn–Sham equations

$$\left(-\frac{1}{2} \nabla_i^2 + v_S(\mathbf{r}) \right) \chi_i = \epsilon_i \chi_i$$

where the effective potential is defined as

$$v_S(\mathbf{r}) = v_J(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})$$

and the exchange–correlation potential is defined through $E_{\text{xc}}[\rho]$ as

$$v_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho}$$

Kohn–Sham DFT V

- 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 $E_{xc}[\rho]$.