

Ensemble DFT

Nikitas I. Gidopoulos

Manchester, 12-13 May 2005

$$H_V \Psi_{V,n} = E_n \Psi_{V,n} \quad n = 0, 1, 2, \dots$$

Rayleigh Ritz minimum principle:

$$\text{Ground state: } E_0 \leq \langle \Psi | H_V | \Psi \rangle, \quad \forall \Psi$$

$$\text{1st exc. state: } E_1 \leq \langle \Psi | H_V | \Psi \rangle, \quad \forall \Psi \perp \Psi_{V,0}$$

Ensemble minimum principle: (Theophilou, 1979; Gross, Oliveira, Kohn, 1988)

$$E_0 + E_1 \leq \langle \Psi | H_V | \Psi \rangle + \langle \Psi' | H_V | \Psi' \rangle, \quad \Psi \perp \Psi'$$

$$\text{Or,} \quad E_0 + E_1 \leq \text{Trace}_{(\Psi, \Psi')} [H_V]$$

Particularly useful for degenerate states.

System with D (almost) degenerate states (lowest)

$$\sum_{n=1}^D \langle \Psi_n | H_V | \Psi_n \rangle = \text{Trace}_{(\Psi_1, \dots, \Psi_D)} [H_V]$$

is a minimum when (Ψ_1, \dots, Ψ_D) span degenerate space $(\Psi_{V,1}, \dots, \Psi_{V,D})$.

For example atom with unfilled shell:

$$\begin{aligned}\Phi_1 &= \frac{1}{\sqrt{(N+1)!}} \text{Det}[\phi_1 \dots \phi_{N_{core}}, \phi_{N+1}] \\ \Phi_2 &= \frac{1}{\sqrt{(N+1)!}} \text{Det}[\phi_1 \dots \phi_{N_{core}}, \phi_{N+2}] \\ &\dots \\ \Phi_D &= \frac{1}{\sqrt{(N+1)!}} \text{Det}[\phi_1 \dots \phi_{N_{core}}, \phi_{N+D}]\end{aligned}$$

Minimising $\text{Trace}_{(\Phi_1, \dots, \Phi_D)}[H_V]$ with respect to spin-orbitals we obtain:

$$\begin{aligned}
& h(\mathbf{r})\phi_i(\mathbf{r}) + \int d^3\mathbf{r}' \frac{\rho_c(\mathbf{r}') + (1/D)\rho_D(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \phi_i(\mathbf{r}) \\
& - \int d^3\mathbf{r}' \frac{\rho_c(\mathbf{r}, \mathbf{r}') + (1/D)\rho_D(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \phi_i(\mathbf{r}') = \sum_{j=1}^{Nc+D} \lambda_{i,j} \phi_j(\mathbf{r}), \quad i = 1 \dots Nc
\end{aligned}$$

$$\begin{aligned}
& h(\mathbf{r})\phi_{N+i}(\mathbf{r}) + \int d^3\mathbf{r}' \frac{\rho_c(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \phi_{N+i}(\mathbf{r}) \\
& - \int d^3\mathbf{r}' \frac{\rho_c(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \phi_{N+i}(\mathbf{r}') = \sum_{j=1}^{Nc+D} \kappa_{i,j} \phi_j(\mathbf{r}), \quad i = 1 \dots D
\end{aligned}$$

$$\rho_c(\mathbf{r}) = \sum_{i=1}^{Nc} |\phi_i(\mathbf{r})|^2 \quad \rho_D(\mathbf{r}) = \sum_{i=1}^D |\phi_{N+i}(\mathbf{r})|^2$$

Inhomogeneous equations arise naturally.

After solving ensemble HF equations, one may diagonalise H_V in degenerate space (Φ_1, \dots, Φ_D)

One can formulate DFT on ensemble ideas

Formulation of DFT on ensemble density ρ^e , not on ground or first excited state densities.

Ensemble $(\Phi, \Phi') \rightarrow$

Ensemble density $\rho^e(\mathbf{r}) = \frac{1}{2}\rho_{\Phi}(\mathbf{r}) + \frac{1}{2}\rho_{\Phi'}(\mathbf{r})$.

Example, Li: $\Phi = 1s^2 2s^{\uparrow}, \Phi' = 1s^2 3s^{\uparrow}$

$$\rho^e(\mathbf{r}) = |\phi_{1s}(\mathbf{r})|^2 + \frac{1}{2}|\phi_{2s}(\mathbf{r})|^2 + \frac{1}{2}|\phi_{3s}(\mathbf{r})|^2$$

Hohenberg -Kohn theorem

Different potentials V, U lead to different ensembles $(\Psi_{V,1}, \Psi_{V,2}), (\Psi_{U,1}, \Psi_{U,2})$.

If $(\Psi_{V,1}, \Psi_{V,2}) = (\Psi_{U,1}, \Psi_{U,2})$, then both H_V and H_U leave space $(\Psi_{V,1}, \Psi_{V,2})$ invariant.

Then $H_V - H_U$ has an eigenstate Ψ in the space $(\Psi_{V,1}, \Psi_{V,2})$.

Hence:

$$\sum_j [V(\mathbf{r}_j) - U(\mathbf{r}_j)] \Psi(\mathbf{r}_1, \sigma_1 \dots \mathbf{r}_N, \sigma_N) = \lambda \Psi(\mathbf{r}_1, \sigma_1 \dots \mathbf{r}_N, \sigma_N)$$

(Impossible!)

Different ensembles $(\Psi_{V,1}, \Psi_{V,2})$, $(\Psi_{U,1}, \Psi_{U,2})$ arising from different potentials V , U lead to different ensemble densities ρ_V^e, ρ_U^e .

Ensemble minimum principle:

$$\text{Trace}_{(\Psi_{V,1}, \Psi_{V,2})}[H_V] < \text{Trace}_{(\Psi_{U,1}, \Psi_{U,2})}[H_V]$$

$$\text{Trace}_{(\Psi_{U,1}, \Psi_{U,2})}[H_U] < \text{Trace}_{(\Psi_{V,1}, \Psi_{U,2})}[H_U]$$

We get:

$$\int d\mathbf{r}[U(\mathbf{r}) - V(\mathbf{r})][\rho_U^e(\mathbf{r}) - \rho_V^e(\mathbf{r})] < 0$$

If $\rho_U^e = \rho_V^e$ then: $0 < 0$.

Constrained search formulation E_V^e : ensemble energy of H_V .

$$E_V^e = \min_{(\Psi, \Psi')} \text{Trace}_{(\Psi, \Psi')} [H_V]$$

In two steps:

Step 1:

$$E_V^e[\rho^e] = \min_{(\Psi, \Psi') \rightarrow \rho^e} \text{Trace}_{(\Psi, \Psi')} [T + W + V]$$

$$E_V^e[\rho] = F^e[\rho] + \int d\mathbf{r} V(\mathbf{r}) \rho^e(\mathbf{r}),$$

$$F^e[\rho] = \min_{(\Psi, \Psi') \rightarrow \rho^e} \text{Trace}_{(\Psi, \Psi')} [T + W],$$

Step 2:

$$E_V^e = \min_{\rho^e \rightarrow N} E_V^e[\rho]$$

At the minimum we have:

$$\frac{\delta}{\delta\rho(\mathbf{r})} \left[F^e[\rho^e] + \int d\mathbf{r} V(\mathbf{r}) \rho^e(\mathbf{r}) - \mu \int d\mathbf{r} \rho^e(\mathbf{r}) \right] = 0$$

$$\left[\frac{\delta F^e[\rho^e]}{\delta\rho(\mathbf{r})} \right]_{\rho_V} = -V(\mathbf{r}) + \mu$$

Ensemble Kohn-Sham scheme

Imagine a system of non-interacting electrons described by an ensemble (Φ, Φ') of Slater determinants, with the same ensemble density ρ_V^e and energy E_V^e . The system lies in an external potential V_s^e .

Aim: determine V_s^e .

$$\begin{aligned}\Phi &= 1/\sqrt{N!} \text{Det}[\phi_1 \dots \phi_{N-1}, \phi_N] \\ \Phi' &= 1/\sqrt{N!} \text{Det}[\phi_1 \dots \phi_{N-1}, \phi_{N+1}]\end{aligned}$$

The orbitals satisfy:

$$\left[-\frac{\nabla^2}{2} + V_s^e(\mathbf{r}) \right] \phi_n(\mathbf{r}) = \epsilon_n \phi_n(\mathbf{r}),$$

$$\rho_V^e(\mathbf{r}) = \sum_{n=1}^{N-1} |\phi_n(\mathbf{r})|^2 + \frac{1}{2}|\phi_N(\mathbf{r})|^2 + \frac{1}{2}|\phi_{N+1}(\mathbf{r})|^2$$

Write:

$$F^e[\rho] = T_s^e[\rho] + \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} + E_{xc}^e[\rho]$$

(Definition of $E_{xc}^e[\rho]$)

We find:

$$V_s^e[\rho](\mathbf{r}) = V(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} + \frac{\delta E_{xc}^e[\rho]}{\delta \rho(\mathbf{r})}$$

To be solved together with

$$\left[-\frac{\nabla^2}{2} + V_s^e(\mathbf{r}) \right] \phi_n(\mathbf{r}) = \epsilon_n \phi_n(\mathbf{r}),$$

$$\rho_V^e(\mathbf{r}) = \sum_{n=1}^{N-1} |\phi_n(\mathbf{r})|^2 + \frac{1}{2} |\phi_N(\mathbf{r})|^2 + \frac{1}{2} |\phi_{N+1}(\mathbf{r})|^2$$

Spurious interactions in the Hartree energy, or exact exchange in ensemble DFT

Take Li: $\Phi = 1s^2 2s^\uparrow$, $\Phi' = 1s^2 3s^\uparrow$

$$\rho^e(\mathbf{r}) = |\phi_{1s}(\mathbf{r})|^2 + \frac{1}{2}|\phi_{2s}(\mathbf{r})|^2 + \frac{1}{2}|\phi_{3s}(\mathbf{r})|^2$$

The Hartree energy is strange!

$$E_H[\rho^e] = \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{\rho^e(\mathbf{r})\rho^e(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}$$

The 2s and the 3s orbitals appear to be interacting electrostatically. We have called this unphysical interaction the ghost interaction:

$$G_H[\rho^e] = \frac{1}{4} \int \int d\mathbf{r} d\mathbf{r}' \frac{|\phi_{2s}(\mathbf{r})|^2 |\phi_{3s}(\mathbf{r}')|^2}{|\mathbf{r}' - \mathbf{r}|}.$$

The corresponding exchange term will be:

$$G_X[\rho^e] = -\frac{1}{4} \int \int d\mathbf{r} d\mathbf{r}' \frac{\phi_{2s}(\mathbf{r}) \phi_{2s}^*(\mathbf{r}') \phi_{3s}(\mathbf{r}') \phi_{3s}^*(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|}.$$

$G_H[\rho]$, $G_X[\rho]$ must be corrected in E_{xc}^e .

We must return to ensemble HF Coulomb direct and exchange energies:

The Coulomb energy for the configurations $\Phi = 1s^2 2s^\uparrow$, $\Phi' = 1s^2 3s^\uparrow$ is:

$$\begin{aligned} \frac{1}{2} \langle \Phi | W | \Phi \rangle + \frac{1}{2} \langle \Phi' | W | \Phi' \rangle &= \frac{1}{2} \int \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \rho^e(\mathbf{r}) \rho^e(\mathbf{r}') \\ &\quad - \frac{1}{2} \int \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \sum_{\sigma} |\rho_{\sigma}^e(\mathbf{r}, \mathbf{r}')|^2 - \underbrace{(G_H[\rho^e] + G_X[\rho^e])}_{G[\rho^e]} \end{aligned}$$

In order to keep the usual definition of the Hartree energy, we must define

$$E_{xc}^e[\rho] = -\frac{1}{2} \int \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \sum_{\sigma} |\rho_{\sigma}^e(\mathbf{r}, \mathbf{r}')|^2 - G[\rho] + E_c^e[\rho]$$

Definition of E_c^e

We may find the functional derivative of E_{xc}^e , G with the OEP method (homogeneous equations) or ...

by varying the orbitals:

We get inhomogeneous eqs. (like ensemble HF)

Departure from usual KS, but correlation can be included.

Current work to calculate ensemble correlation energy for uniform electron gas.

Atom	Ensemble	Dim	$E_c = 0$ $G = 0$	$E_c = 0$ G	Exper
He	$\{1s^2\}^1S$; $\{1s2s\}^1S$	2	-66.531	-67.456	-68.705
He	$\{1s2s\}^3S$; $\{1s3s\}^3S$	2	-57.143	-57.606	-57.744
He	$\{1s2s\}^3S$; $\{1s2p\}^3P$	2	-58.096	-58.613	-58.621
He	$\{1s2s\}^3S$; $\{1s2p\}^3P$	4	-57.932	-58.313	-58.335
Li	$\{1s^22s\}^2S$; $\{1s^22p\}^2P$	4	-200.463	-200.953	-202.100
Li	$\{1s^22s\}^2S$; $\{1s^23s\}^2S$	2	-199.946	-200.382	-201.799
C^{2+}	$\{1s^22s^2\}^1S$; $\{1s^22s2p\}^3P$	4	-985.392	-986.616	-989.278

Atom	Ensemble	Dim	CS $G = 0$	CS G	Exper
He	$\{1s^2\}^1S$; $\{1s2s\}^1S$	2	-67.565	-68.463	-68.705
He	$\{1s2s\}^3S$; $\{1s3s\}^3S$	2	-57.143	-57.606	-57.744
He	$\{1s2s\}^3S$; $\{1s2p\}^3P$	2	-58.096	-58.613	-58.621
He	$\{1s2s\}^3S$; $\{1s2p\}^3P$	4	-57.932	-58.313	-58.335
Li	$\{1s^22s\}^2S$; $\{1s^22p\}^2P$	4	-201.797	-202.287	-202.100
Li	$\{1s^22s\}^2S$; $\{1s^23s\}^2S$	2	-201.253	-201.661	-201.799
C^{2+}	$\{1s^22s^2\}^1S$; $\{1s^22s2p\}^3P$	4	-988.113	-989.310	-989.278

Summary:

One may formulate ensemble HF equations (inhomogeneous) particularly suited for degenerate systems.

One may formulate ensemble KS equations (homogeneous) but also inhomogeneous (HF + correlations) again appropriate for degenerate systems

For finite systems it makes sense to diagonalise H_V to obtain “dynamical fluctuations” between degenerate states.

For extended systems what is the corresponding coupling operator that could be diagonalised??

Work in progress to calculate LDA for ensemble correlation energy