Center for Molecular Modeling

Computational Materials Physics

Department of Materials Science and Engineering

1st Hohenberg-Kohn theorem

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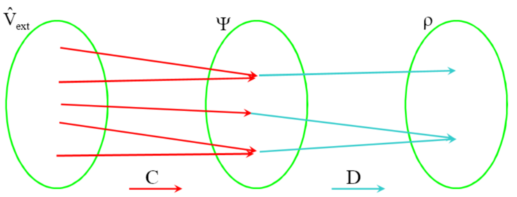
http://molmod.ugent.be
http://www.ugent.be/ea/dmse/en
my talks on Youtube: http://goo.gl/P2b1Hs

1st Hohenberg-Kohn theorem

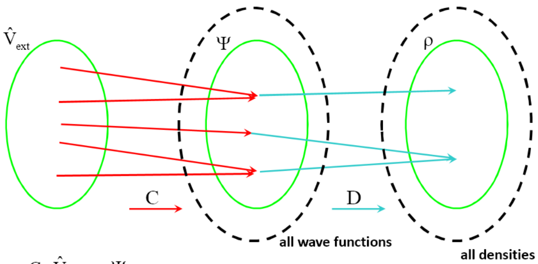


$C : \hat{V}_{ext} \mapsto \Psi$ surjective by construction

$D : \Psi \mapsto \rho$ surjective by construction

Are C and D also injective ?

Note : mind the definition of these sets



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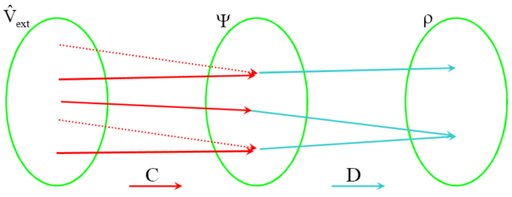

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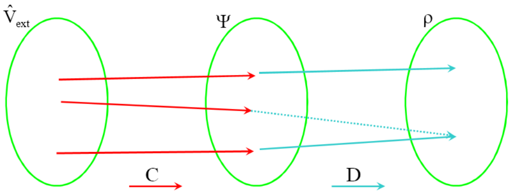
1st Hohenberg-Kohn theorem



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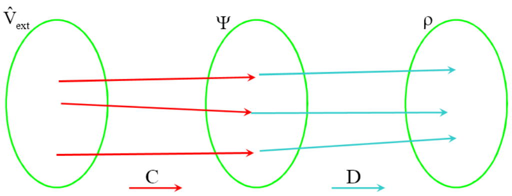
1st Hohenberg-Kohn theorem



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proof: 1^{st} Hohenberg-Kohn theorem

(for non-degenerate ground states)

To proof: if $\Psi \neq \Psi'$, then $\rho \neq \rho'$
Do this by assuming that $\Psi \neq \Psi'$ and $\rho = \rho'$, which will lead to a contradiction.

Ψ is the ground state of a hamiltonian H, ground state energy is E_{gs}
Ψ' is the ground state of a hamiltonian H', ground state energy is E'_{gs}

Same number of electrons (otherwise trivial), hence:
H = T + W +V and H' = T + W + V' ➔ H = H' – V' + V

Due to variational principle:

$$E_{gs} = \langle \Psi | H | \Psi \rangle < \langle \Psi' | H | \Psi' \rangle = \langle \Psi' | H' + V - V' | \Psi' \rangle = E'_{gs} + \int \rho'(\bar{r}) \left[v(\bar{r}) - v'(\bar{r}) \right] d\bar{r}$$

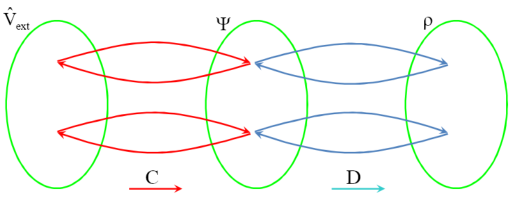
Repeat argument, starting with Ψ' :

$$E'_{gs} < E_{gs} + \int \rho(\bar{r}) \left[v'(\bar{r}) - v(\bar{r}) \right] d\bar{r}$$

Add, assuming that $\rho = \rho'$ ➔ $E_{gs} + E'_{gs} < E_{gs} + E'_{gs}$ ➔ contradiction

P. Hohenberg and W. Kohn, Phys. Rev. 136B (1964) 864

1^{st} Hohenberg-Kohn theorem



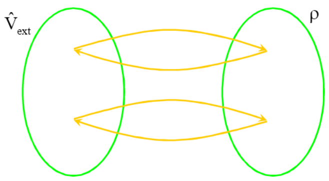
$C : \hat{V}_{ext} \mapsto \Psi$ bijective

$D : \Psi \mapsto \rho$ bijective

$\Rightarrow$ one-to-one relations

1^{st} Hohenberg-Kohn theorem

" There is a one-to-one correspondence between the ground state density of a many-electron system and the external potential. "



Consequence: any observable ground state property of the many-electron system can be written as a unique functional of the density :

$$\text{property} = \langle \Psi | \hat{O} | \Psi \rangle = O[\rho]$$