Computational Materials Physics

Center for Molecular Modeling

Department of Materials Science and Engineering

the electron density

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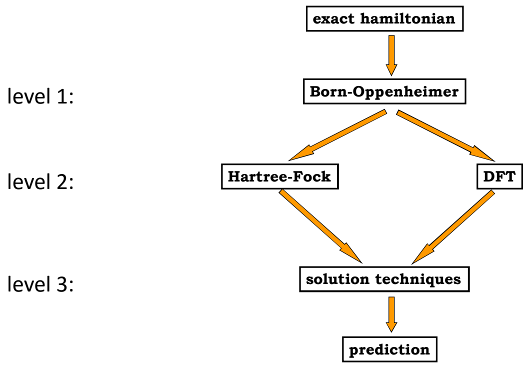
http://molmod.ugent.be
http://www.ugent.be/ea/dmse/en
my talks on Youtube: http://goo.gl/P2b1Hs

three levels of approximations



electron density for 1 electron

The electron density operator for one electron :

$$\hat{\rho}(\vec{r}) = \delta(\vec{r}\,' - \vec{r})$$

The electron density for one electron :

$$\begin{aligned}\rho(\vec{r}) &= \langle \Psi | \hat{\rho}(\vec{r}) | \Psi \rangle \\ &= \int \Psi^*(\vec{r}\,')\Psi(\vec{r}\,')\delta(\vec{r}\,' - \vec{r})\,d\vec{r}\,' \\ &= \Psi^*(\vec{r})\Psi(\vec{r}) \\ &= |\Psi(\vec{r})|^2\end{aligned}$$

Interpretation: probability to find the electron at $\vec{r}$

electron density for N electrons

The electron density operator for N electrons :

$$\hat{\rho}(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{r}\,' - \vec{r})$$

The electron density for N electrons :

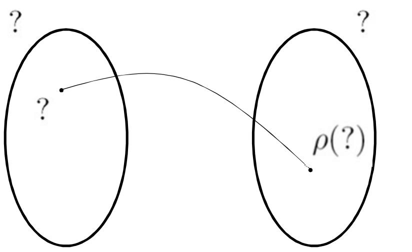
$$\begin{aligned}\rho(\vec{r}) &= \left\langle \Psi \middle| \hat{\rho}(\vec{r}) \middle| \Psi \right\rangle \\ &= \sum_{i=1}^{N} \int \Psi^{*}(\vec{r}_1,\ldots,\vec{r}_i \equiv \vec{r},\ldots,\vec{r}_N)\,\Psi(\vec{r}_1,\ldots,\vec{r}_i \equiv \vec{r},\ldots,\vec{r}_N)\,d\vec{r}_1 \ldots \cancel{d\vec{r}_i} \ldots d\vec{r}_N \\ &= \sum_{i=1}^{N} \left|\varphi(\vec{r}_i)\right|^2 \quad (*)\end{aligned}$$

Interpretation: probability to find any electron at $\vec{r}$, regardless where the N-1 other are.

(*) : only if Ψ can be written by one-electron wave functions φ.

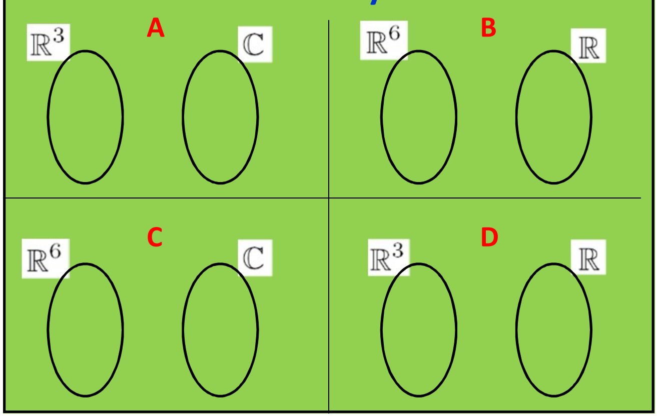
the electron density is a function

$$\rho : ? \mapsto ? : ? \mapsto \rho(?)$$



Exercise:
two spin-less particles

the electron density is a function



the electron density is a function

spoiler
prevention