

Density functional theory in solid state physics

Lecture 3

- Pauli exclusion principle: Approximations to the many-body wavefunction need to be anti-symmetric with respect to particle exchange

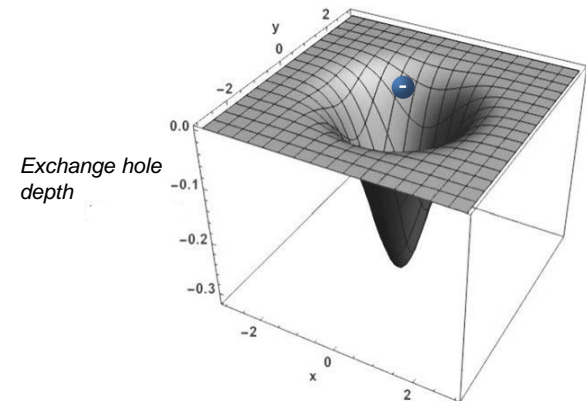
Hartree → Hartree-Fock equations:

$$\left(-\sum_i^N \nabla_i^2 + v(\vec{r}) + \underbrace{\int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'}_{\text{Hartree potential } v^H} \right) \varphi_{i,s_i}(\vec{r}) - \underbrace{\sum_j \delta_{s_i,s_j} \int \frac{\varphi_{j,s_j}^*(\vec{r}') \varphi_{i,s_i}(\vec{r}') \varphi_{j,s_j}(\vec{r})}{|\vec{r} - \vec{r}'|} d\vec{r}'}_{\text{Exchange term}} = \varepsilon_{i,s_i} \varphi_{i,s_i}(\vec{r})$$

- Decreased probability of finding another electron with same spin in the vicinity of a given electron

→ Exchange hole

- Hartree-Fock is successful for atoms, the eigenvalues ε_{i,s_i} correspond to discrete „energy levels“ that can be used to derive ionization and excitation energies („Janak’s theorem“)



- On the other hand: The Hartree-Fock equations do not include other electron-electron interaction effects that are important in large molecules and solids. HF is also computationally expensive in such systems
- $X\alpha$ method: replace the exchange component the Hartree-Fock equations by a simpler effective potential based on the homogeneous electron gas

$$v^{X\alpha}(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{3}{2} \frac{k_F(\vec{r})}{\pi} \alpha$$

- Thomas-Fermi theory: approximate kinetic energy of Schrödinger equation with kinetic electron-density dependent kinetic energy of homogeneous electron gas

$$T[n] = \frac{3h^2}{10m} \left(\frac{3}{8\pi} \right)^{\frac{2}{3}} \int [n(\vec{r})]^{5/3} dr$$

$$E^{TF}[n] = T[n] + \int \underbrace{v^{eff}(\vec{r})}_{v(\vec{r}) + v^H(\vec{r}) + v^{X\alpha}(\vec{r})} n(\vec{r}) dr$$

e.g. $v(\vec{r}) + v^H(\vec{r}) + v^{X\alpha}(\vec{r})$

- Obtain electron density from a given external potential $v(\vec{r})$

- Density functional theory: Extension of the idea proposed by Thomas and Fermi
- Is it possible to formulate an *exact* many-body quantum-mechanical theory completely in terms of $n(\vec{r})$? Yes
- The two theorems introduced by Hohenberg and Kohn in 1964 form the theoretical basis of modern density functional theory

PHYSICAL REVIEW

VOLUME 136, NUMBER 3B

9 NOVEMBER 1964

Inhomogeneous Electron Gas*

P. HOHENBERG†

École Normale Supérieure, Paris, France

AND

W. KOHN‡

École Normale Supérieure, Paris, France and Faculté des Sciences, Orsay, France

and

University of California at San Diego, La Jolla, California

(Received 18 June 1964)

This paper deals with the ground state of an interacting electron gas in an external potential $v(\mathbf{r})$. It is proved that there exists a universal functional of the density, $F[n(\mathbf{r})]$, independent of $v(\mathbf{r})$, such that the expression $E = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$ has as its minimum value the correct ground-state energy associated with $v(\mathbf{r})$. The functional $F[n(\mathbf{r})]$ is then discussed for two situations: (1) $n(\mathbf{r}) = n_0 + \tilde{n}(\mathbf{r})$, $\tilde{n}/n_0 < 1$, and (2) $n(\mathbf{r}) = \varphi(\mathbf{r}/r_0)$ with φ arbitrary and $r_0 \rightarrow \infty$. In both cases F can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of these methods are presented.

First Hohenberg-Kohn theorem

- First Hohenberg-Kohn theorem: „The ground state density $n(\vec{r})$ determines the external potential $v(\vec{r})$ to within a trivial additive constant“
- Let us consider a stationary many-body system with energy $E = T + V + U$, a many-body wavefunction ψ , and a Hamiltonian $\hat{H} = \hat{T} + \hat{V} + \hat{U}$, where

(from here on, every term will be expressed in atomic units, i.e. $\hbar = m = e = 4\pi\epsilon_0 = 1$)

$$\hat{T} = \frac{1}{2} \sum_i \nabla_i^2 \quad \rightarrow \quad T = \frac{1}{2} \sum_i \langle \psi | \nabla_i^2 | \psi \rangle \quad (\text{kinetic energy})$$

$$\hat{V} = \sum_i v(\vec{r}_i) \quad \rightarrow \quad V = \int v(\vec{r}) n(\vec{r}) d\vec{r} \quad (\text{electron-nuclei interaction})$$

$$\hat{U} = \frac{1}{2} \sum_i \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \quad \rightarrow \quad U = \frac{1}{2} \sum_i \sum_{i \neq j} \left\langle \psi \left| \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \right| \psi \right\rangle \quad (\text{electron-electron interaction})$$

- \hat{T} and \hat{U} are considered as „universal“ terms
- the external potential $v(\vec{r})$ determines the Hamiltonian of the system, and correspondingly ψ and E

- The ground state electronic density

$$n_0(\vec{r}) = \langle \psi | \hat{n} | \psi \rangle$$

density operator

is clearly a functional of $v(\vec{r})$, as $(v \rightarrow \hat{H} \rightarrow \psi \rightarrow n)$

- We want to show that the opposite direction is valid as well, i.e. that, conversely, $v(\vec{r})$ is a unique functional of $n_0(\vec{r})$ (+a trivial additive constant)
- Assumption in the following: the groundstate is non-degenerate, i.e. there is a unique groundstate many-body wavefunction ψ for a particular external potential $v(\vec{r})$ (and thus also for the Hamiltonian \hat{H})

First Hohenberg-Kohn theorem

- Proof by *reductio ad absurdum*
- We know that the potential $v(\vec{r})$ gives rise to the groundstate density $n_0(\vec{r})$
- Let us now assume that there is another potential $v'(\vec{r})$ that gives rise to the exact same ground state density $n_0(\vec{r})$:

$$\hat{H}\psi = (\hat{T} + \hat{V} + \hat{U}) \psi = E\psi$$

$$\hat{H}'\psi' = (\hat{T} + \hat{V}' + \hat{U}) \psi' = E'\psi'$$

- What if $v'(\vec{r})$ differs from $v(\vec{r})$ by a constant shift A ?

$$\langle \psi' | \hat{H}' | \psi' \rangle = \langle \psi' | \hat{H} + A | \psi' \rangle = \langle \psi' | \hat{H} | \psi' \rangle + A \underbrace{\langle \psi' | \psi' \rangle}_{=1}$$

→ ψ' is also ground state wavefunction of \hat{H} , i.e. $\psi' = \psi$

- If $v'(\vec{r})$ differs from $v(\vec{r})$ by more than a constant shift A , then $\psi \neq \psi'$.

As the ground state is non-degenerate, the following statements have to be true

$$\begin{aligned} \blacksquare \quad \langle \psi | \hat{H} | \psi \rangle < \langle \psi' | \hat{H} | \psi' \rangle &\quad \rightarrow \quad E < E' + \underbrace{\langle \psi' | (\hat{V} - \hat{V}') | \psi' \rangle}_{= \int (v(\vec{r}) - v'(\vec{r})) n_0(\vec{r}) d\vec{r}} \end{aligned}$$

$$\begin{aligned} \blacksquare \quad \langle \psi' | \hat{H}' | \psi' \rangle < \langle \psi | \hat{H}' | \psi \rangle &\quad \rightarrow \quad E' < E + \underbrace{\langle \psi | (\hat{V}' - \hat{V}) | \psi \rangle}_{= \int (v'(\vec{r}) - v(\vec{r})) n_0(\vec{r}) d\vec{r}} \end{aligned}$$

- Adding these two statements leads to the inconsistency

$$E + E' < E + E'$$

- Thus, $v(\vec{r})$ is (up to a constant shift) a unique functional of the ground state density $n_0(\vec{r})$

- Corrolary: Since, in turn, $v(\vec{r})$ determines \hat{H} , the many-body wavefunctions ψ (ground state and excited states) are unique functionals of $n_0(\vec{r})$ as well.
- All properties that are derivable from solution of the Schrödinger Equation are thus completely determined by the ground state density $n_0(\vec{r})$.
- For example:
 - The many-body wavefunctions of the ground and excited states $\psi_m(\vec{r}_1, \dots, \vec{r}_N)$
 - The Green's functions $G(\vec{r}_1 t_1, \dots, \vec{r}_N t_N)$
 - The response functions $\chi(\vec{r}, \vec{r}', \omega)$
 - All observables of the form $O[n] = \langle \psi[n] | \hat{O} | \psi[n] \rangle$
- This means that we, in principle, do not have to deal with the $3N$ coordinates of the many-body wavefunction in order to build the exact Hamiltonian of the system, but the 3 coordinates of the electron density are sufficient.

Second Hohenberg-Kohn theorem


- Second theorem of Hohenberg-Kohn: One can define a universal functional for the energy $E[n]$ in terms of the electron density $n(\vec{r})$, which is valid for any external potential.

The electron density that minimizes the energy of this functional is the true ground state electron density corresponding to the full solution of the Schrödinger equation

- Corrolary: This gives access to properties related to the electronic ground state of a given system, but excited state properties need to be determined in other ways.
- Kinetic and electron-electron energy are uniquely defined by $n(\vec{r})$, thus we can define a total energy functional

$$E_{HK}[n] = \underbrace{T[n] + U[n]}_{F_{HK}[n]} + \int v(\vec{r})n(\vec{r})dr + E_{n-n}$$

Interaction between electrons Interaction between nuclei



- F_{HK} is a universal functional of the density, the same for all electronic systems
- The Hohenberg-Kohn functional F_{HK} is defined only for densities that can be generated by an external potential $v(\vec{r})$.
„ v -representable“

Second Hohenberg-Kohn theorem

- Let's consider a system with external potential $v(\vec{r})$, ground state wavefunction ψ and ground state density $n_0(\vec{r})$. Due to the first HK theorem:

$$\langle \psi | \hat{H} | \psi \rangle = E = E_{HK}[n_0]$$

- For a different density n' (and thus a different many-body wavefunction ψ'), we get

$$\begin{aligned} \langle \psi' | \hat{H} | \psi' \rangle &= E' = E_{HK}[n'] \\ &> \langle \psi | \hat{H} | \psi \rangle = E_{HK}[n_0] \end{aligned}$$

- $E_{HK}[n]$ evaluated for the ground state density n_0 is lower than the value for any other density
- Minimizing $E_{HK}[n]$ with respect to $n(\vec{r})$ allows finding the exact ground state density and the corresponding energy
- Problem: $F_{HK}[n]$ is unknown

- A more general proof: constrained search formulation by Levy and Lieb [1,2]

- Start with the general expression for the total energy.

[1] *Proc. Natl. Acad. Sci. U.S.A.* 76, 6062 (1979)
[2] *Int. Jour. Quant. Chem.* 24, 243-277 (1983)

$$E[\psi] = \langle \psi | \hat{T} | \psi \rangle + \langle \psi | \hat{U} | \psi \rangle + \int v(\vec{r}) n(\vec{r}) dr + E_{n-n}$$

- One now considers only wavefunctions that give the same density $n(r)$. The total energy of the system is then a functional of the density,

$$E_{LL}[n] = \underbrace{\min_{\psi \rightarrow n(r)} [\langle \psi | \hat{T} | \psi \rangle + \langle \psi | \hat{U} | \psi \rangle]}_{F_{LL}[n]} + \int v(\vec{r}) n(\vec{r}) dr + E_{n-n}$$

- The Levy-Lieb functional is defined for any density that can be generated from a N-particle wavefunction ψ_N „N-representable“
- The ground state can then be found by variation of the density as opposed to variation of ψ .
- This formulation provides an operational definition for the universal density functional F and is valid for degenerate ground states as well.

- Both Hohenberg-Kohn and Levy-Lieb prove that a formulation of the exact total energy in terms of the electron density n is possible
- The HK (and LL) theorems do not provide any practical method to actually derive those energy functionals
- Problem: How to express T and U in terms of the electron density?

$$F_{HK}[n] = T[n] + U[n]$$

- Hohenberg-Kohn (1964): Separate the classical Coulomb energy from the functional F_{HK}

$$F_{HK}[n] = \frac{1}{2} \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}d\vec{r}' + G[n]$$

Hartree energy

another universal functional.

To be found or to be approximated

- Approximating $G[n]$ with T_{TF} : Thomas-Fermi model

$$E_{TF}[n] = \underbrace{\frac{1}{2} \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}d\vec{r}'}_{F_{TF}[n]} + T_{TF}[n] + \int v(\vec{r})n(\vec{r})d\vec{r} (+E_{n-n})$$

Problem: the approximation of the kinetic energy is too severe

- A different route: the Hartree method

$$\left(-\frac{1}{2} \nabla_i^2 + v(\vec{r}) + \underbrace{\int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'}_{v_H(\vec{r})} - v_{SIC}(\vec{r}) \right) \varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r})$$

$$E[\{\varphi_i\}] = T_S[\{\varphi_i\}] + V[n] + E_H[n] + E_{SIC}[\{\varphi_i\}]$$

- SCF procedure: Search for an approximate electron density that minimizes the total energy
- The Hartree equations model electrons that move independently in an effective potential $v_{eff}(\vec{r}) = v(\vec{r}) + v_H(\vec{r}) - v_{SIC}(\vec{r})$ given by the other electrons (and the nuclei).
- The identity of the other electrons is lost.
- The kinetic energy of the system is approximated by the kinetic energy of independent particles, $T_S[\{\varphi_i\}]$
- Observation: The Hartree equations follow from the HK formalism for a homogeneous electron gas of non-interacting electrons moving in the effective potential v_{eff} .

- The kinetic energy of an interacting system is not T_S , but has an additional contribution from electron exchange and other correlation effects
- Ansatz by Kohn and his post-doc Lu Sham (1965):

$$G[n] = T_S[n] + E_{XC}[n]$$

Kinetic energy of a system of non-interacting electrons with density n

Energy functional that contains exchange and correlation interaction of a system of interacting electrons with density n

- This leads to the total energy expression

$$E_{KS}[n] = T_S[n] + \int v(\vec{r})n(\vec{r})dr + E_{n-n} + \frac{1}{2} \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} drdr' + E_{XC}[n]$$

- Advantage: The expression for the kinetic energy of non-interacting electrons is known exactly, even though it only implicitly depends on the electron density,

$$T_S[\{\varphi_i[n]\}] = \sum_i^N \int \varphi_i^* \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \varphi_i dr$$

- Assumption: Electrons can be described in terms of single-particle wavefunctions φ_i and an electron density

$$n(\vec{r}) = \sum_i n_i |\varphi_i(\vec{r})|^2$$

Occupation of orbital i

- Based on this, one can follow the approach used for the Hartree- or Hartree-Fock method to derive a set of equations to find the ground state density.
- Using a variational approach to minimize the energy functional with respect to the density n ,

$$\frac{\delta}{\delta n} \left(E_{KS}[n] - \underbrace{\mu \left(\int n(\vec{r}) d\vec{r} - N \right)}_{\text{conservation of the particle number}} \right) = 0$$

leads to the expression $\mu = \frac{\delta T_S[n]}{\delta n} + v_{KS}[n]$

with the effective potential $v_{KS}(\vec{r}) = v(\vec{r}) + v_H(\vec{r}) + v_{XC}(\vec{r})$

and the *exchange-correlation potential* $v_{XC}(\vec{r}) = \frac{\delta E_{XC}[n]}{\delta n}$

- Alternatively: we can also minimize the energy functional with respect to the single-electron wavefunctions:

$$\frac{\delta}{\delta\varphi_i^*(\vec{r})} \left(E_{KS}[n] - \underbrace{\sum_j \varepsilon_j (\langle\varphi_i|\varphi_j\rangle - \delta_{ij})}_{\text{orthonormality of } \varphi_i} \right) = 0$$

- This exploits that T_S is not a direct functional of $n(\vec{r})$, but of the single-electron orbitals
- Using the chain-rule, we arrive at the following set of equations (one per φ_i^*)

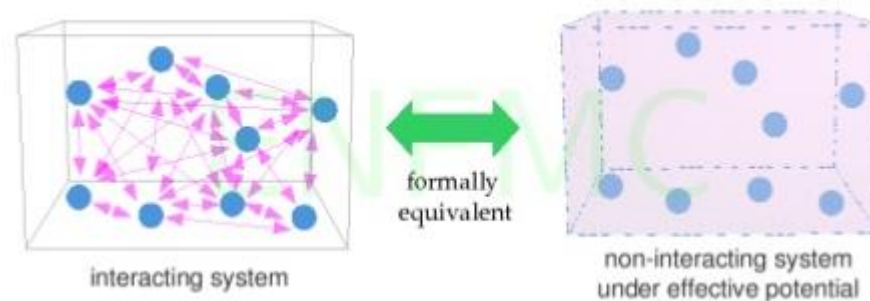
$$\frac{\delta T_{KS}}{\delta\varphi_i^*(\vec{r})} + \underbrace{\left(\frac{\delta E_{e-n}[n]}{\delta n(\vec{r})} + \frac{\delta E_H[n]}{\delta n(\vec{r})} + \frac{\delta E_{XC}[n]}{\delta n(\vec{r})} \right)}_{v_{KS}} \frac{\delta n(\vec{r})}{\delta\varphi_i^*(\vec{r})} - \frac{\delta}{\delta\varphi_i^*(\vec{r})} \left(\sum_j \varepsilon_j (\langle\varphi_i|\varphi_j\rangle - \delta_{ij}) \right) = 0$$

Kohn-Sham mapping

- In analogy to the Hartree or Hartree-Fock equations, one can then obtain the ground state density $n_0(\vec{r})$ simply by solving the single-particle equations

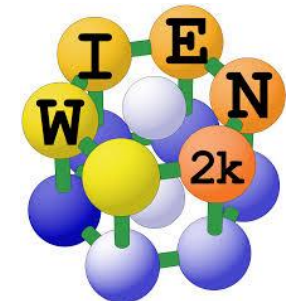
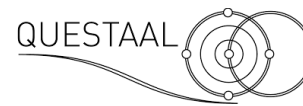
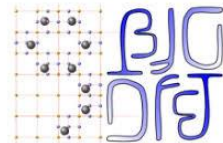
$$\left(-\frac{1}{2} \nabla^2 + v_{KS}(\vec{r}) \right) \varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r})$$

- These equations are known nowadays as the *Kohn-Sham equations*
- We model the system as a fictitious system of non-interaction electrons moving in an auxiliary potential $v_{KS}(r) = v(r) + v_H(r) + v_{XC}(r)$
- $v_{KS}(r)$ maps the real, interacting, system onto the auxiliary non-interacting system such that the non-interacting system reproduces the physical properties of the interacting system.



DFT codes using the Kohn-Sham approach

- The Kohn-Sham equations are not the only (or necessarily best!) approach for practical implementations of DFT, but it is by far the most dominant.
- A large number of computational packages using Kohn-Sham DFT is readily available nowadays



...and many more!

- In analogy to the Hartree or Hartree-Fock equations, one can then obtain the ground state density $n_0(\vec{r})$ simply by solving the single-particle equations

$$\left(-\frac{1}{2}\nabla^2 + v(\vec{r}) + \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + v_{XC}(\vec{r}) \right) \varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r})$$

- Advantage of the Kohn-Sham approach: The first three terms are known exactly
- All approximations have been pushed in the final term, the exchange-correlation potential
- For the exact $v_{XC}(\vec{r})$, the electron density obtained from minimizing the Kohn-Sham equations is the exact ground state electron density $n_0(\vec{r})$ and all derived quantities are exact.
- v_{XC} is the central approximation in modern (Kohn-Sham) density functional theory not known exactly.

- For Hartree-Fock, Janak's theorem stated that differences between the eigenvalues have a physical meaning
- Is there a meaning for the eigenvalues of the Kohn-Sham equations?
- In principle, the eigenvalues have no intrinsic physical meaning
- One exception: the highest occupied eigenvalue of a finite system (atom, molecule,...) is equal to the negative of the ionization energy - if the electron density is exact [1]
- In practice, the KS eigenvalues ε_i are used as single-electron energies in a band structure picture or as input for other theories
- Slater-Janak theorem [2]: eigenvalue of state i is the derivative of E_{tot} with respect to the occupation of state i

$$\begin{aligned}\varepsilon_i &= \frac{dE_{tot}}{dn_i} = \int \frac{dE_{tot}}{dn(\vec{r})} \frac{dn(\vec{r})}{dn_i} dr \\ &= \int \frac{dT_S}{dn(\vec{r})} \frac{dn(\vec{r})}{dn_i} dr + \int (v(\vec{r}) + v_H(\vec{r}) + v_{XC}(\vec{r})) \frac{dn(\vec{r})}{dn_i} dr\end{aligned}$$

For non-interacting systems:

$$E_{tot} = \sum_i n_i \varepsilon_i$$

Slater-Janak „transition state“: $I \approx -\varepsilon_i$ for which $n_i=1/2$

[1] Phys. Rev. A 30, 2745 (1984)
[2] Phys. Rev. B 18, 7165 (1978)

- The exchange-correlation potential and energy contain all the electron interaction effects that goes beyond the classical Coulomb interaction in the Hartree term

$$E_{XC} = E_X + E_C$$

Exchange component: imposes effects arising from the Pauli exclusion principle

Correlation component: all other quantum mechanical electron-electron correlation effects. For example quantum fluctuations in the electron density

- Common: express E_{XC} in terms of an exchange-correlation density $\varepsilon_{XC}([n], \vec{r})$

$$E_{XC}[n] = \int n(r) \varepsilon_{XC}([n(\vec{r})], \vec{r}) dr$$

- The exchange-correlation potential is then

$$v_{XC}(\vec{r}) = \frac{dE_{XC}}{dn(\vec{r})} = \varepsilon_{XC}([n], \vec{r}) + n(\vec{r}) \frac{d\varepsilon_{XC}([n], \vec{r})}{dn(\vec{r})}$$

response to changes in the density

- Some relevant known properties of the exact exchange-correlation functional:
 - The exact E_{XC} can be written in terms of the exchange-correlation hole $n_{XC} = n_X + n_C$:

$$E_{XC} = \iint n(\vec{r}) \frac{n_{XC}(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}'$$

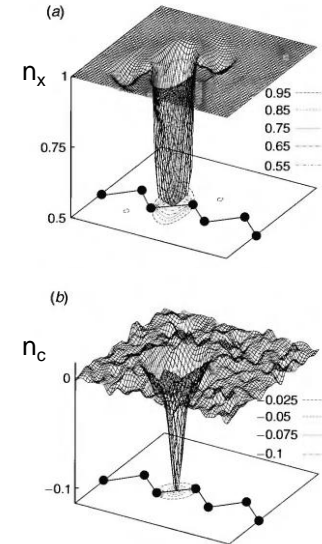
The exchange-correlation hole contains a charge of $+e$:

$$\int n_X(\vec{r}, \vec{r}') d\vec{r}' = -1$$

$$\int n_C(\vec{r}, \vec{r}') d\vec{r}' = 0$$

$n_{XC}(\vec{r}, \vec{r}')$ can be explicitly calculated for atoms and (much more tediously) for solids

A powerful path to approximating E_{XC} and v_{XC} is modelling the exchange-correlation hole



Phys. Rev. B 57, 8972 (1998)

- For a one-electron system with density $n(\vec{r}) = \varphi^*(\vec{r})\varphi(\vec{r})$, the exchange-correlation functional is equal to the exchange component of the Hartree-Fock approximation:

$$E_X[n] = -\frac{1}{2} \iint \frac{\varphi^*(\vec{r})\varphi^*(\vec{r}')\varphi(\vec{r}')\varphi(\vec{r})}{|\vec{r} - \vec{r}'|} d\vec{r}d\vec{r}' = -\frac{1}{2} \iint \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}d\vec{r}'$$

$$E_C[n] = 0$$

In general, the exact exchange-correlation potential cancels the self-interaction in the Hartree potential

The exchange energy in Hartree-Fock is exact, but difficult (if possible) to write as a functional in terms of the electron density.

- In finite systems (such as atoms or molecules), the exact v_{XC} decreases asymptotically with $v_{XC} \sim \frac{1}{r}$ for $r \rightarrow \infty$
- The exact exchange-correlation potential exhibits a „derivative discontinuity“ with respect to particle numbers

For a (possibly non-integer) particle number n with $N \leq n \leq N + 1$:

$$E_n = E_N + (n - N)(E_{N+1} - E_N)$$

Energy of the system with n electrons

i.e. the exact exchange-correlation potential „jumps“ when adding or removing an electron from the system

This has implications for the accuracy of predicted electronic band gaps

