

# Density functional theory in solid state physics

## Lecture 2

- RRZE can create accounts on the HPC for the purpose of doing the DFT exercises later in the semester
- They require a list with the IdM identifiers of all participants that want accounts
- Let me know if you do not want your identifier to be forwarded to the RRZE

- Exact theoretical treatment of quantum-mechanical systems in principle known
- Problem: Electrons in a many-body system are correlated (i.e. interact with each other)
- Exact inclusion of electron-electron interaction makes the Schrödinger Eq. completely intractable for systems larger than small atoms.
- Hartree approximation: Approximate the many-body wavefunction by a product of  $N$  single-electron states (Hartree product)

$$\psi_e(\vec{r}_1, \dots, \vec{r}_j, \dots, \vec{r}_N) = \varphi_{\sigma_1}(\vec{r}_1) \varphi_{\sigma_2}(\vec{r}_2) \dots \varphi_{\sigma_j}(\vec{r}_j) \dots \varphi_{\sigma_N}(\vec{r}_N)$$

- The problem then decomposes into  $N$  single-particle Schrödinger equations

$$\left( -\frac{\hbar^2}{2m_e} \nabla_i^2 + V^{e-ion}(\vec{r}) + \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' - V_{SIC}(\vec{r}) \right) \varphi_i(\vec{r}) = \epsilon_i \varphi_i(\vec{r})$$

With the electron density

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

and the self-interaction correction

$$V_{SIC}(\vec{r}) = -\frac{e^2}{4\pi\epsilon_0} \int \frac{|\varphi_i(\vec{r})|^2}{|\vec{r} - \vec{r}'|} d\vec{r}'$$

- Pauli exclusion principle: No two fermions (i.e. particles with half-integer spin) in an atom, molecule or solid can have the same set of quantum numbers.

The many-body wavefunction of fermions needs to be anti-symmetric with respect to interchange of *any* two electron coordinates, i.e.

$$\psi_e(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_j, \dots, \vec{r}_N) = -\psi_e(\vec{r}_j, \vec{r}_2, \dots, \vec{r}_1, \dots, \vec{r}_N)$$

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- We can include spin, for example, through definition of single-electron „spin-orbitals“

$$\chi_{i,s_i}(v_i) = \varphi_{i,s_i}(\vec{r}_i) \alpha_{s_i}(\omega_i)$$

Spatial part

Spin part

with „space-spin“ coordinates  $v_i = (\vec{r}_i, \omega_i)$

Spin quantum number, (for now)  
takes values  $s_i = \uparrow$  or  $s_i = \downarrow$

and the spin functions  $\alpha_{\uparrow}(\omega) = \begin{cases} 1, & \text{if } \omega = 1 \\ 0, & \text{if } \omega = 2 \end{cases}$  and  $\alpha_{\downarrow}(\omega) = \begin{cases} 0, & \text{if } \omega = 1 \\ 1, & \text{if } \omega = 2 \end{cases}$

- The Hartree product does not satisfy the required antisymmetry

e.g. for two particles:  $\psi_e(v_1, v_2) = \chi_{1,s_1}(v_1) \chi_{2,s_2}(v_2)$

$$\psi_e(v_2, v_1) = \chi_{1,s_1}(v_2) \chi_{2,s_2}(v_1)$$

$$\psi_e(v_1, v_2) \stackrel{!}{=} -\psi_e(v_2, v_1) \rightarrow \chi_{1,s_1}(v_2) \chi_{2,s_2}(v_1) \stackrel{!}{=} -\chi_{1,s_1}(v_1) \chi_{2,s_2}(v_2)$$

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Not generally the case

# Slater determinant

- The Hartree product does not satisfy the required antisymmetry

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Not generally the case

- We can approximate the exact antisymmetric many-body wavefunction of the system by a Slater determinant

$$\psi_e \approx \Phi_{sl}(v_1, v_2, \dots, v_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_{1,s_1}(v_1) & \cdots & \chi_{N,s_N}(v_1) \\ \vdots & \ddots & \vdots \\ \chi_{1,s_1}(v_N) & \cdots & \chi_{N,s_N}(v_N) \end{vmatrix}$$

Normalization of  $\Phi_{sl}$

- Assumptions:  $\langle \chi_{i,s_i}(v_i) | \chi_{j,s_j}(v_j) \rangle = \sum_{\omega, \omega'} \iint \chi_{i,s_i}(v_i) \chi_{j,s_j}(v_j) dr_i dr_j = \delta_{i,j} \delta_{s_i,s_j}$



# Slater determinant

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- Assumptions:  $\langle \chi_{i,s_i}(v_i) | \chi_{j,s_j}(v_j) \rangle = \sum_{\omega, \omega'} \iint \chi_{i,s_i}(v_i) \chi_{j,s_j}(v_j) \mathrm{d}r_i \mathrm{d}r_j = \delta_{i,j} \delta_{s_i,s_j}$
- Check for a two-electron system:  $\psi_e(v_1, v_2) = \frac{1}{\sqrt{2}} (\chi_{1,s_1}(v_1) \chi_{2,s_2}(v_2) - \chi_{1,s_1}(v_2) \chi_{2,s_2}(v_1))$   
 $= -\psi_e(v_2, v_1)$

- The exact wavefunction can be expanded over Slater determinants containing all possible one-electron wavefunctions

$$\psi_e = \sum_{\mu} c_{\mu} \Phi_{sl,\mu}(v_1, v_2, \dots, v_N)$$

- In selected cases,  $\Phi_{sl}(v_1, v_2, \dots, v_N)$  is the exact many-body wavefunction

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- Probability density of two electrons with coordinates  $v_1$  and  $v_2$ :

$$\rho(v_1, v_2) = \int |\Phi_{sl}|^2 dv_3 \dots dv_N$$

$$\propto \sum_{k,l} \left[ |\chi_{k,s_k}(\vec{r}_1, \omega_1)|^2 |\chi_{l,s_l}(\vec{r}_2, \omega_2)|^2 - \chi_{k,s_k}(\vec{r}_1, \omega_1) \chi_{l,s_l}(\vec{r}_2, \omega_2) \chi_{k,s_k}(\vec{r}_2, \omega_2) \chi_{l,s_l}(\vec{r}_1, \omega_1) \right]$$

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- If  $\chi_{k,s_k}$  and  $\chi_{l,s_l}$  have opposite spin, the second term vanishes and the spin orbitals are uncorrelated

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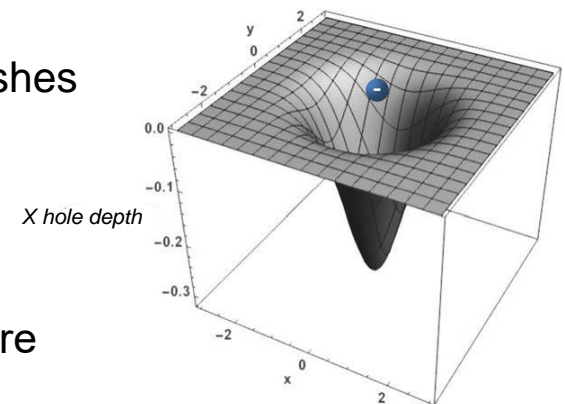
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- If  $\chi_{k,s_k}$  and  $\chi_{l,s_l}$  have opposite spin, the second term vanishes and the spin orbitals are uncorrelated
- If they are of equal spin,  $\rho(v_1, v_2)=0$  for  $\vec{r}_1 = \vec{r}_2$ .

Every electron is surrounded by an „exchange hole“, where electrons of similar spin are not (or hardly) found



# Hartree-Fock energy

- We use only one Slater determinant, but which one? A: We want the „best“ one.
- Put  $\Phi_{sl}$  into Schrödinger Equation:

$$\begin{aligned}
 E &= \langle \Phi_{sl} | \hat{H}_e | \Phi_{sl} \rangle \\
 &= \langle \Phi_{sl} | -\frac{\hbar^2}{2m_e} \sum_i^N \nabla_i^2 + \sum_i^N \underbrace{\sum_I^M \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{R}_I|}}_{v(\vec{r}_i)} + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{i,j \neq i}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} | \Phi_{sl} \rangle
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(2)
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(1) (2) (3)

- Example: Two-electron system

$$\blacksquare \langle \Phi_{sl} | -\frac{\hbar^2}{2m_e} \sum_i^2 \nabla_i^2 | \Phi_{sl} \rangle = \frac{1}{2} \sum_{\omega_1, \omega_2} \iint (\chi_{1,v_1}^* \chi_{2,v_2}^* - \chi_{1,v_2}^* \chi_{2,v_1}^*) \left( -\frac{\hbar^2}{2m_e} \sum_i^2 \nabla_i^2 \right) \overbrace{(\chi_{1,v_1} \chi_{2,v_2} - \chi_{1,v_2} \chi_{2,v_1})}^{\chi_{1,s_1}(v_1)} dr_1 dr_2$$

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 &= \frac{1}{2} \sum_{\omega_1} \int \chi_{1,v_1}^* \left( -\frac{\hbar^2}{2m_e} \sum_i^2 \nabla_i^2 \right) \chi_{1,v_1} dr_1 \underbrace{\sum_{\omega_2} \int \chi_{2,v_2}^* \chi_{2,v_2} dr_2}_{=1} \\
 &\quad + \frac{1}{2} \sum_{\omega_1} \int \chi_{2,v_1}^* \left( -\frac{\hbar^2}{2m_e} \sum_i^2 \nabla_i^2 \right) \chi_{2,v_1} dr_1 \sum_{\omega_2} \int \chi_{1,v_2}^* \chi_{1,v_2} dr_2 \\
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$$\begin{aligned}
 \blacksquare \left\langle \Phi_{sl} \left| -\frac{\hbar^2}{2m_e} \sum_i^2 \nabla_i^2 \right| \Phi_{sl} \right\rangle &= \frac{1}{2} \sum_{\omega_1, \omega_2} \iint (\chi_{1,v_1}^* \chi_{2,v_2}^* - \chi_{1,v_2}^* \chi_{2,v_1}^*) \left( -\frac{\hbar^2}{2m_e} \sum_i^2 \nabla_i^2 \right) \overbrace{(\chi_{1,s_1}(v_1) \chi_{2,v_2} - \chi_{1,v_2} \chi_{2,s_1})}^{\chi_{1,s_1}(v_1)} dr_1 dr_2 \\
 &= \frac{1}{2} \sum_{\omega_1} \int \chi_{1,v_1}^* \left( -\frac{\hbar^2}{2m_e} \sum_i^2 \nabla_i^2 \right) \chi_{1,v_1} dr_1 \underbrace{\sum_{\omega_2} \int \chi_{2,v_2}^* \chi_{2,v_2} dr_2}_{=1} \\
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 &= -\frac{\hbar^2}{2m_e} \sum_i \sum_{\omega} \langle \chi_{i,v_i} | \nabla_i^2 | \chi_{i,v_i} \rangle = -\frac{\hbar^2}{2m_e} \sum_i \langle \varphi_{i,s_i} | \nabla_i^2 | \varphi_{i,s_i} \rangle
 \end{aligned}$$

$\uparrow$   
 $\sum_{\omega} \alpha_{s_i}^*(\omega) \alpha_{s_i}(\omega) = 1$

# Hartree-Fock energy

- $\langle \Phi_{sl} | \sum_i^2 v(\vec{r}_i) | \Phi_{sl} \rangle = \frac{1}{2} \sum_{\omega_1, \omega_2} \iint (\chi_{1,v_1}^* \chi_{2,v_2}^* - \chi_{1,v_2}^* \chi_{2,v_1}^*) (\sum_i^2 v(\vec{r}_i)) (\chi_{1,v_1} \chi_{2,v_2} - \chi_{1,v_2} \chi_{2,v_1}) dr_1 dr_2$

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# Hartree-Fock energy

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 \blacksquare \quad \langle \Phi_{sl} | \sum_i^2 v(\vec{r}_i) | \Phi_{sl} \rangle &= \frac{1}{2} \sum_{\omega_1, \omega_2} \iint (\chi_{1,v_1}^* \chi_{2,v_2}^* - \chi_{1,v_2}^* \chi_{2,v_1}^*) (\sum_i^2 v(\vec{r}_i)) (\chi_{1,v_1} \chi_{2,v_2} - \chi_{1,v_2} \chi_{2,v_1}) dr_1 dr_2 \\
 &= \frac{1}{2} \sum_{\omega_1} \int \chi_{1,v_1}^* v(\vec{r}_1) \chi_{1,v_1} dr_1 + \sum_{\omega_1} \int \chi_{2,v_1}^* v(\vec{r}_1) \chi_{2,v_1} dr_1 + [v(\vec{r}_2) \text{ terms}] \\
 &= \sum_{\omega} \int v(\vec{r}) \left( \chi_{1,s_1}^* (\vec{r}, \omega) \chi_{1,s_1} (\vec{r}, \omega) + \chi_{2,s_2}^* (\vec{r}, \omega) \chi_{2,s_2} (\vec{r}, \omega) \right) dr \\
 &= \int v(\vec{r}) \underbrace{\sum_i^2 |\varphi_{i,s_i}(\vec{r})|^2}_{=n(\vec{r})} dr = \int v(\vec{r}) n(\vec{r}) dr
 \end{aligned}$$

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 &= \sum_{\omega} \int v(\vec{r}) \left( \chi_{1,s_1}^*(\vec{r}, \omega) \chi_{1,s_1}(\vec{r}, \omega) + \chi_{2,s_2}^*(\vec{r}, \omega) \chi_{2,s_2}(\vec{r}, \omega) \right) dr \\
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 \end{aligned}$$

$$\begin{aligned}
 \blacksquare \quad \left\langle \Phi_{sl} \left| \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right| \Phi_{sl} \right\rangle &= \frac{1}{2} \sum_{\omega_1, \omega_2} \iint (\chi_{1,v_1}^* \chi_{2,v_2}^* - \chi_{1,v_2}^* \chi_{2,v_1}^*) \left( \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right) (\chi_{1,v_1} \chi_{2,v_2} - \chi_{1,v_2} \chi_{2,v_1}) dr_1 dr_2 \\
 &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\omega_1, \omega_2} \iint \frac{|\chi_{1,v_1}|^2 |\chi_{2,v_2}|^2 + |\chi_{2,v_1}|^2 |\chi_{1,v_2}|^2}{|\vec{r}_1 - \vec{r}_2|} dr_1 dr_2 \\
 &\quad - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\omega_1, \omega_2} \iint \frac{\chi_{1,v_1}^* \chi_{2,v_2} \chi_{1,v_2} \chi_{2,v_1} + \chi_{2,v_1}^* \chi_{1,v_2} \chi_{1,v_1} \chi_{2,v_2}}{|\vec{r}_1 - \vec{r}_2|} dr_1 dr_2
 \end{aligned}$$

$$\begin{aligned}
 \blacksquare \quad \langle \Phi_{sl} | \sum_i^2 v(\vec{r}_i) | \Phi_{sl} \rangle &= \frac{1}{2} \sum_{\omega_1, \omega_2} \iint (\chi_{1,v_1}^* \chi_{2,v_2}^* - \chi_{1,v_2}^* \chi_{2,v_1}^*) (\sum_i^2 v(\vec{r}_i)) (\chi_{1,v_1} \chi_{2,v_2} - \chi_{1,v_2} \chi_{2,v_1}) d\vec{r}_1 d\vec{r}_2 \\
 &= \frac{1}{2} \sum_{\omega_1} \int \chi_{1,v_1}^* v(\vec{r}_1) \chi_{1,v_1} d\vec{r}_1 + \sum_{\omega_1} \int \chi_{2,v_1}^* v(\vec{r}_1) \chi_{2,v_1} d\vec{r}_1 + [v(\vec{r}_2) \text{ terms}] \\
 &= \sum_{\omega} \int v(\vec{r}) \left( \chi_{1,s_1}^*(\vec{r}, \omega) \chi_{1,s_1}(\vec{r}, \omega) + \chi_{2,s_2}^*(\vec{r}, \omega) \chi_{2,s_2}(\vec{r}, \omega) \right) d\vec{r} \\
 &= \int v(\vec{r}) \underbrace{\sum_i^2 |\varphi_{i,s_i}(\vec{r})|^2}_{=n(\vec{r})} d\vec{r} = \int v(\vec{r}) n(\vec{r}) d\vec{r}
 \end{aligned}$$

$$\begin{aligned}
 \blacksquare \quad \left\langle \Phi_{sl} \left| \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right| \Phi_{sl} \right\rangle &= \frac{1}{2} \sum_{\omega_1, \omega_2} \iint (\chi_{1,v_1}^* \chi_{2,v_2}^* - \chi_{1,v_2}^* \chi_{2,v_1}^*) \left( \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right) (\chi_{1,v_1} \chi_{2,v_2} - \chi_{1,v_2} \chi_{2,v_1}) d\vec{r}_1 d\vec{r}_2 \\
 &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\omega_1, \omega_2} \iint \frac{|\chi_{1,v_1}|^2 |\chi_{2,v_2}|^2 + |\chi_{2,v_1}|^2 |\chi_{1,v_2}|^2}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \\
 &\quad - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\omega_1, \omega_2} \iint \underbrace{\frac{\chi_{1,v_1}^* \chi_{2,v_2} \chi_{1,v_2} \chi_{2,v_1} + \chi_{2,v_1}^* \chi_{1,v_2} \chi_{1,v_1} \chi_{2,v_2}}{|\vec{r}_1 - \vec{r}_2|}}_{\sum_i \sum_{j \neq i} \frac{\chi_{i,v_i}^* \chi_{j,v_j}^* \chi_{i,v_j} \chi_{j,v_i}}{|\vec{r}_1 - \vec{r}_2|}} d\vec{r}_1 d\vec{r}_2
 \end{aligned}$$

■

$$\begin{aligned}
 \square \quad \left\langle \Phi_{sl} \left| \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right| \Phi_{sl} \right\rangle &= \frac{1}{2} \sum_{\omega_1, \omega_2} \iint (\chi_{1,v_1}^* \chi_{2,v_2}^* - \chi_{1,v_2}^* \chi_{2,v_1}^*) \left( \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right) (\chi_{1,v_1} \chi_{2,v_2} - \chi_{1,v_2} \chi_{2,v_1}) dr_1 dr_2 \\
 &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\omega_1, \omega_2} \iint \frac{|\chi_{1,v_1}|^2 |\chi_{2,v_2}|^2 + |\chi_{2,v_1}|^2 |\chi_{1,v_2}|^2}{|\vec{r}_1 - \vec{r}_2|} dr_1 dr_2 \\
 &\quad + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\omega_1, \omega_2} \iint \frac{|\chi_{1,v_1}|^2 |\chi_{1,v_2}|^2 + |\chi_{2,v_1}|^2 |\chi_{2,v_2}|^2}{|\vec{r}_1 - \vec{r}_2|} dr_1 dr_2 \\
 &\quad - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\omega_1, \omega_2} \iint \frac{|\chi_{1,v_1}|^2 |\chi_{1,v_2}|^2 + |\chi_{2,v_1}|^2 |\chi_{2,v_2}|^2}{|\vec{r}_1 - \vec{r}_2|} dr_1 dr_2 \\
 &\quad - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\omega_1, \omega_2} \sum_i \sum_{j \neq i} \iint \frac{\chi_{i,v_1}^* \chi_{j,v_2}^* \chi_{i,v_2} \chi_{j,v_1}}{|\vec{r}_1 - \vec{r}_2|} dr_1 dr_2
 \end{aligned}$$



# Hartree-Fock energy

$$\begin{aligned}
 \blacksquare \quad \langle \Phi_{sl} | \sum_i^2 v(\vec{r}_i) | \Phi_{sl} \rangle &= \frac{1}{2} \sum_{\omega_1, \omega_2} \iint (\chi_{1,v_1}^* \chi_{2,v_2}^* - \chi_{1,v_2}^* \chi_{2,v_1}^*) (\sum_i^2 v(\vec{r}_i)) (\chi_{1,v_1} \chi_{2,v_2} - \chi_{1,v_2} \chi_{2,v_1}) d\vec{r}_1 d\vec{r}_2 \\
 &= \frac{1}{2} \sum_{\omega_1} \int \chi_{1,v_1}^* v(\vec{r}_1) \chi_{1,v_1} d\vec{r}_1 + \sum_{\omega_1} \int \chi_{2,v_1}^* v(\vec{r}_1) \chi_{2,v_1} d\vec{r}_1 + [v(\vec{r}_2) \text{ terms}] \\
 &= \sum_{\omega} \int v(\vec{r}) \left( \chi_{1,s_1}^*(\vec{r}, \omega) \chi_{1,s_1}(\vec{r}, \omega) + \chi_{2,s_2}^*(\vec{r}, \omega) \chi_{2,s_2}(\vec{r}, \omega) \right) d\vec{r} \\
 &= \int v(\vec{r}) \underbrace{\sum_i^2 |\varphi_{i,s_i}(\vec{r})|^2}_{=n(\vec{r})} d\vec{r} = \int v(\vec{r}) n(\vec{r}) d\vec{r}
 \end{aligned}$$
  

$$\begin{aligned}
 \blacksquare \quad \left\langle \Phi_{sl} \left| \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right| \Phi_{sl} \right\rangle &= \frac{1}{2} \sum_{\omega_1, \omega_2} \iint (\chi_{1,v_1}^* \chi_{2,v_2}^* - \chi_{1,v_2}^* \chi_{2,v_1}^*) \left( \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right) (\chi_{1,v_1} \chi_{2,v_2} - \chi_{1,v_2} \chi_{2,v_1}) d\vec{r}_1 d\vec{r}_2 \\
 &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\omega_1, \omega_2} \iint \frac{|\chi_{1,v_1}|^2 |\chi_{2,v_2}|^2 + |\chi_{2,v_1}|^2 |\chi_{1,v_2}|^2}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \\
 &\quad + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\omega_1, \omega_2} \iint \frac{|\chi_{1,v_1}|^2 |\chi_{1,v_2}|^2 + |\chi_{2,v_1}|^2 |\chi_{2,v_2}|^2}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \\
 &\quad - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\omega_1, \omega_2} \iint \frac{|\chi_{1,v_1}|^2 |\chi_{1,v_2}|^2 + |\chi_{2,v_1}|^2 |\chi_{2,v_2}|^2}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \\
 &\quad - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\omega_1, \omega_2} \sum_i \sum_{j \neq i} \iint \frac{\chi_{i,v_1}^* \chi_{j,v_2}^* \chi_{i,v_2} \chi_{j,v_1}}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \\
 &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \iint \frac{n(\vec{r}_1) n(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{i,j} \iint \sum_{\omega_1, \omega_2} \frac{\chi_{i,v_1}^* \chi_{j,v_2}^* \chi_{i,v_2} \chi_{j,v_1}}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \\
 &\quad \underbrace{\frac{\varphi_{i,s_i}^*(\vec{r}_1) \varphi_{j,s_j}^*(\vec{r}_2) \varphi_{i,s_i}(\vec{r}_2) \varphi_{j,s_j}(\vec{r}_1)}{|\vec{r}_1 - \vec{r}_2|}}
 \end{aligned}$$

- For N-electron system:

$$E^{HF} = T[\{\varphi_{\sigma_i, s_i}\}] + E^{el-ion}[n] + E^H[n] + E^X[\{\varphi_{\sigma_i, s_i}\}] \geq E^0 \quad E^0: \text{exact total energy}$$

with

$$T[\{\varphi_{\sigma_i, s_i}\}] = -\frac{\hbar^2}{2m_e} \sum_i \langle \varphi_{\sigma_i, s_i} | \nabla_i^2 | \varphi_{\sigma_i, s_i} \rangle \quad \text{Kinetic energy}$$

$$E^{el-ion}[n] = \int v(\vec{r}) n(\vec{r}) d\vec{r} \quad \text{Electron-nuclei interaction energy}$$

$$E^H[n] = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \iint \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' \quad \text{Hartree energy}$$

$$E^X[\{\varphi_{\sigma_i, s_i}\}] = -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{i,j} \delta_{s_i, s_j} \iint \frac{\varphi_{i, s_i}^*(\vec{r}) \varphi_{j, s_j}^*(\vec{r}') \varphi_{i, s_i}(\vec{r}') \varphi_{j, s_j}(\vec{r})}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' \quad \text{Exchange energy}$$

- The exchange energy effectively lowers the electrostatic repulsion energy between electrons of opposite spin

- The best approximation to  $\psi_e$  should be given by using set  $\{\varphi_{\sigma_i, s_i}\}$  that minimizes  $E^{HF}$
- Variational approach:

- Define functional  $Q = E^{HF}[\{\varphi_{i, s_i}^*, \varphi_{i, s_i}\}] + \underbrace{\sum_{i,j} \left( \lambda_{i, s_i, j, s_j} - \langle \varphi_{i, s_i} | \varphi_{j, s_j} \rangle \right)}_{\text{Normalization constraint with Lagrange multipliers } \lambda}$

- We are looking for a set of orbitals for which Q is a minimum, i.e. that satisfy

$$\frac{\delta Q}{\delta \varphi_{i, s_i}^*(\vec{r})} = 0$$

- This leads to the so-called „Hartree-Fock equations“ (neglecting all the prefactors)

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

- For  $i=j$ , the additional exchange term cancels self-interaction effects from the Hartree potential

- The energy required to remove an electron from state  $k$  from an  $N$  electron system is

$$\Delta I_k = E_k^{N-1} - E^N$$

Total energy of a system of  $N-1$  electrons  
With the  $k$ th state being unoccupied

$$E_k^{N-1} = \langle \psi_{e,k}^{N-1} | H^{N-1} | \psi_{e,k}^{N-1} \rangle$$

Total energy of a the ground state of a system of  $N$  electrons

$$E^N = \langle \psi_e^N | H^N | \psi_e^N \rangle$$

- We can calculate both energies  $E_k^{N-1}$  and  $E^N$  under the assumptions that
  - We use the Hartree-Fock approximation, i.e. a single Slater determinant
  - The orbitals  $\varphi_{i,s_i}$  do not change significantly when removing the electron
  - The removal is so fast that the nuclei cannot react in time

- This leads to (again neglecting all the prefactors)

$$\begin{aligned} \Delta I_k &\approx \langle \Phi_{sl,k}^{N-1} | H^{HF,N-1} | \Phi_{sl,k}^{N-1} \rangle - \langle \Phi_{sl}^N | H^{HF,N-1} | \Phi_{sl}^N \rangle \\ &\vdots \\ &\approx -\langle \varphi_{k,s_k} | H^{HF} | \varphi_{k,s_k} \rangle = -\varepsilon_{k,s_k} \end{aligned}$$

- Correspondingly, the energy difference between and occ. state  $k$  and unocc. state  $l$  is:

$$\Delta E^{i \rightarrow j} \approx \varepsilon_{l,s_l} - \varepsilon_{k,s_k} \quad \text{„Koopman's theorem“}$$

- We can also write the exchange term as 
$$v_i^x(\vec{r})\varphi_{i,s_i}(\vec{r}) = -\frac{e^2}{4\pi\epsilon_0} \int \frac{n_i^{HF}(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} dr' \varphi_{i,s_i}(\vec{r})$$

With the pair density 
$$n_i^{HF}(\vec{r}, \vec{r}') = \sum_j \delta_{s_i, s_j} \frac{\varphi_{j,s_j}^*(\vec{r}')\varphi_{i,s_i}(\vec{r}')\varphi_{j,s_j}(\vec{r})}{\varphi_{i,s_i}(\vec{r})}$$

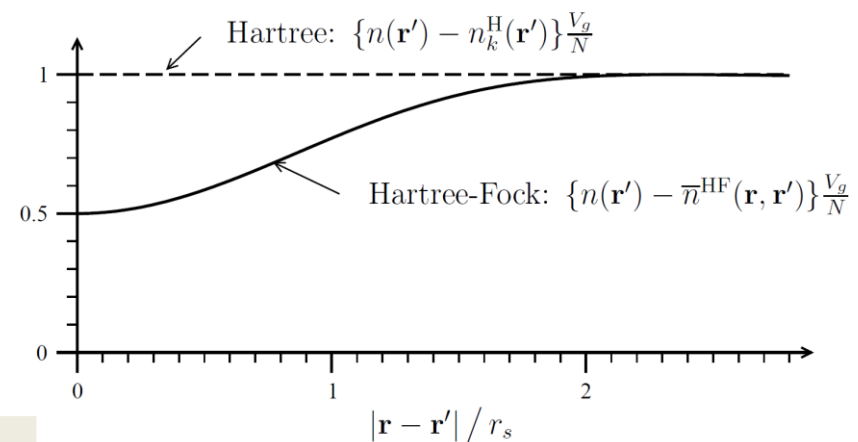
- Compare to SIC in Hartree approximation: 
$$v_i^{SIC}(\vec{r}) = -\frac{e^2}{4\pi\epsilon_0} \int \frac{n_i^H(\vec{r}')}{|\vec{r} - \vec{r}'|} dr', n_i^H(\vec{r}') = |\varphi_{i,s_i}|^2$$
- In contrast to  $v^H$ ,  $v^x$  is different for each electron

- $n^{HF}$  contains exactly one electron:

$$\int n_i^{HF}(\vec{r}, \vec{r}') dr' = 1$$

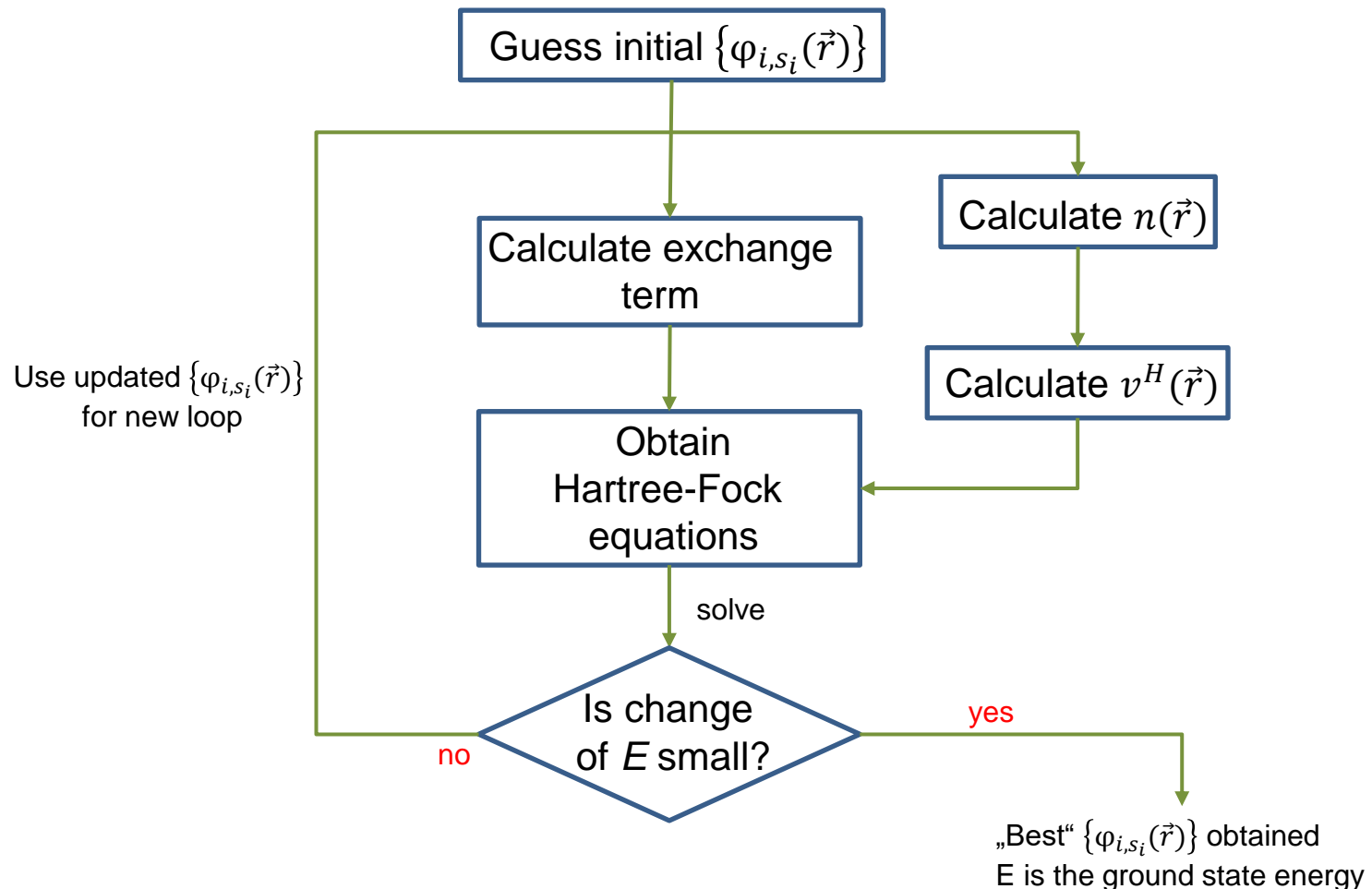
- $n^{HF}$  corresponds to the exchange hole, which is non-existent in the Hartree approximation

For a homogenous electron gas:



# The SCF method

- As for the Hartree method, one can solve the effective single-particle system given by the Hartree-Fock equations iteratively by using the „self-consistent field“ method



## Hartree-Fock, pros and cons

- The Hartree-Fock method is widely implemented in quantum chemistry packages and the foundation of more elaborate „post-Hartree-Fock“ methods
- These methods are among the go-to-methods for the prediction of the properties of molecules.

Freely accessible codes with Hartree-Fock implementation:



- Advantages of the Hartree-Fock method
  - Clear improvement over Hartree approximation
  - Exact inclusion of exchange interaction between electrons (Pauli correlation)
  - Naturally self-interaction free
  - Good results for atoms, groundstate and excitation energies

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## ENERGIES OF ATOMS AND IONS CALCULATED BY THE HARTREE-FOCK METHOD

**Yu. B. Malykhanov\* and M. V. Gorshunov**

UDC 539.184

*Energies of atoms from hydrogen to calcium and all their ions up to the one-electron atom inclusively that were calculated in the algebraic approximation of the Hartree–Fock method were compared with the experimental values obtained from ionization potentials. It was established that the calculated energies of atoms and atoms with  $5 < Z \leq 20$  were only 0.3–0.5% greater than the experimental values. This indicated that the approximations underlying the Hartree–Fock method were correct.*



- Advantages of the Hartree-Fock method
  - Clear improvement over Hartree approximation
  - Exact inclusion of exchange interaction between electrons (Pauli correlation)
  - Naturally self-interaction free
  - Good results for atoms, groundstate and excitation energies
- Disadvantages
  - The exchange term is expensive to compute for larger systems, for example larger molecules or solids.
  - Electronic correlation effects due to Coulomb repulsion between electrons is only included in an averaged way. Such effects are particularly important in solids.

- The exchange term makes Hartree-Fock computationally expensive for larger systems
- $X\alpha$  method<sup>1</sup>: replacement of the non-local exchange term by a simplified *local* term
- Starting point is the homogenous electron gas. In this case, all single-particle states are planewaves

$$\varphi_{j,s_j}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}_j \cdot \vec{r}}$$

- The exchange term then becomes

$$\begin{aligned} v_k^x(r) &= -\frac{e^2}{4\pi\epsilon_0} \int \frac{n_i^{HF}(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' = -\frac{e^2}{4\pi\epsilon_0} \int \sum_j^N \delta_{s_i s_j} \frac{\varphi_{j,s_j}^*(\vec{r}') \varphi_{i,s_i}(\vec{r}') \varphi_{j,s_j}(\vec{r})}{\varphi_{i,s_i}(\vec{r}) |\vec{r} - \vec{r}'|} d\vec{r}' \\ &= -\frac{e^2}{4\pi\epsilon_0} \frac{1}{(2\pi)^3} \int_0^{k_F} \int \frac{e^{i(\vec{k}' - \vec{k}) \cdot (\vec{r}' - \vec{r})}}{|\vec{r} - \vec{r}'|} d\vec{r}' dk' \end{aligned} \quad \text{With } \sum_j^N \delta_{s_i s_j} \rightarrow \frac{V}{(2\pi)^3} \int_0^{k_F} dk'$$

∴ *Fourier transformation*

$$= -\frac{e^2}{4\pi\epsilon_0} \frac{2k_F}{\pi} F\left(\frac{k}{k_F}\right) \quad \text{with } F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right|$$

[1] Phys. Rev. 81, 385 (1951); 82, 5381 (1951)

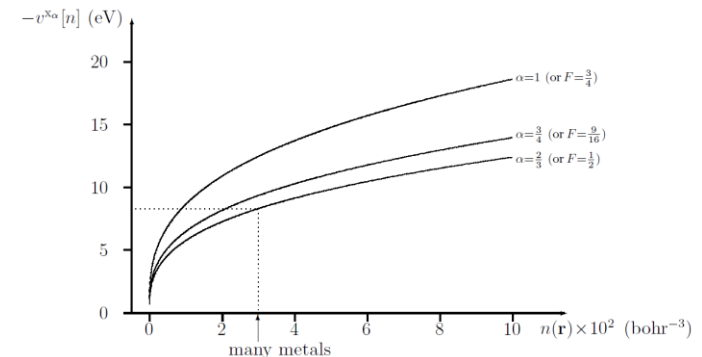
$$v_k^x(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{2k_F}{\pi} F\left(\frac{k}{k_F}\right) \quad \text{with } F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right|$$

- State independent potential: average  $v_k^x(r)$  over  $k$ :

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

With a position-dependent Fermi wave number  $k_F(\vec{r}) = \sqrt[3]{3\pi^2 n(\vec{r})}$   
and  $\alpha = \frac{4}{3} \bar{F}$

- What value for  $\alpha$ ?      Averaging over all occupied states :  $\bar{F}=0.5$   
Averaging over all states close to  $k_F$  :  $\bar{F}=0.75$
- An empirical value  $\alpha = 0.7$  was proposed to best fit experimental results**      Slater himself proposed  $\alpha = 1$
- The  $X\alpha$  method in many cases gives better results than Hartree-Fock for solids than Hartree-Fock
- Semiempirical inclusion of Coulomb repulsion (screening) that is largely absent in HF?



- Do we really need to use wavefunctions to derive a material's physics properties?
- Motivation: many observables are determined by the electron density. For example scattering, bonding etc. The density should be a function of the potential  $v^{eff}(\vec{r})$
- Thomas-Fermi theory: semi-classical approach centered around the electron density  $n(\vec{r})$  as an approximation of

$$\left( -\frac{\hbar^2}{2m} \sum_i^N \nabla_i^2 + v^{eff}(\vec{r}) \right) \varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r})$$

- Idea: Assume that we have an electron gas with homogenous or slowly varying electron density, i.e. it has to be nearly constant within a small volume  $\Delta V$
- The energy of the highest energy electron is then equal to the chemical potential:

$$\frac{\hbar^2}{2m} k_F^2(\vec{r}) + v^{eff}(\vec{r}) = \mu \quad (\text{Thomas-Fermi Eq.})$$

With a position-dependent Fermi wave number  $k_F(\vec{r}) = \sqrt[3]{3\pi^2 n(\vec{r})}$

- From knowledge of  $\mu$  and  $v^{eff}(\vec{r})$ , one can deduct  $n(\vec{r})$  without wavefunctions.

- Kinetic energy density at  $\vec{r}$ :

$$\begin{aligned} t[n(\vec{r})] &= \frac{1}{V} \int_0^{k_F} \frac{\hbar^2}{2m} k^2 dN = \frac{1}{V} \int_0^{k_F} \frac{\hbar^2}{2m} k^2 \left( 2 \cdot 4\pi k^2 \frac{V}{8\pi^3} \right) dk \\ &= \frac{3\hbar^2}{10m} \left( \frac{3}{8\pi} \right)^{\frac{2}{3}} [n(\vec{r})]^{5/3} \end{aligned}$$

- Density-dependent kinetic energy expression for all electrons in the system:

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

- Thomas-Fermi total energy

$$\begin{aligned} E^{TF}[n] &= T[n] + \int \underbrace{v^{eff}(\vec{r})}_{\text{e.g. } v(\vec{r}) + v^H(\vec{r}) + v^{X\alpha}(\vec{r})} n(\vec{r}) d\vec{r} \end{aligned}$$

- Density can also be obtained from variational ansatz

- Advantages of the Thomas-Fermi theory
  - Exact theory for atoms with infinite nuclear charge
  - Simple and elegant model, does not require wavefunctions
  - Naturally includes the exclusion principle and Coulomb repulsion
  - Starting point for the description of electron screening
  - Starting point for more elaborate theories

# Examples for versatility of TF model principles

## PHYSICAL REVIEW LETTERS

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### Bound for the Kinetic Energy of Fermions Which Proves the Stability of Matter

Elliott H. Lieb\*

*Departments of Mathematics and Physics, Princeton University, Princeton, New Jersey 08540*

and

Walter E. Thirring

*Institut für Theoretische Physik der Universität Wien, A-1090 Wien, Austria*

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We first prove that  $\sum |e(V)|$ , the sum of the negative energies of a single particle in a potential  $V$ , is bounded above by  $(4/15\pi) \int |V|^{5/2}$ . This, in turn, implies a lower bound for the kinetic energy of  $N$  fermions of the form  $\frac{1}{2}(3\pi/4)^{2/3} \int \rho^{5/3}$ , where  $\rho(x)$  is the one-particle density. From this, using the no-binding theorem of Thomas-Fermi theory, we present a short proof of the stability of matter with a reasonable constant for the bound.

## THE PHYSICAL REVIEW

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### Thomas-Fermi Theory of Nuclei\*

H. A. BETHE

*Laboratory of Nuclear Studies, Cornell University, Ithaca, New York*

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A Thomas-Fermi theory of large, finite nuclei is developed. Realistic nuclear forces with repulsive core are assumed, and maximum use is made of the theory of nuclear matter. Simplifications are introduced wherever permissible. The local-density approximation with a certain correction is found to be valid. Tensor forces are replaced by a density-dependent, effective central force, the repulsive core by a density-dependent  $\delta$ -function interaction. The Thomas-Fermi expression for kinetic energy is shown to be good whenever the density is at least 17% of nuclear-matter density; under the same conditions, the Slater approximation to the mixed density  $\rho(r, \rho_2)$  is valid. From the total energy of the nucleus, an integral equation is derived for the density  $\rho(r)$ . This is approximated by a differential equation which is solved analytically. The resulting density distribution has both similarities with and differences from the conventional, Fermi-type distribution. Our density agrees as well with electron-scattering experiments as the Fermi type does. The thickness of the nuclear surface comes out about 19% too large from our theory; the surface energy is in good agreement with the semiempirical value. So far, the number of neutrons and protons has been assumed equal, and the Coulomb force has been neglected.

### Thomas-Fermi Description of Incoherent Light Scattering from an Atomic-Trap BEC

Eddy Timmermans and Paolo Tommasini

*Institute for Theoretical Atomic and Molecular Physics*

*Harvard-Smithsonian Center for Astrophysics*

*Cambridge, MA 02138*

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### Abstract

We present a Thomas-Fermi treatment of resonant incoherent scattering of low-intensity light by a dilute spatially confined Bose-Einstein condensate. The description gives simple analytical results and allows scattering data from finite-size condensates to be interpreted in terms of the properties of the homogeneous BEC-system. As an example, we show how the energy dispersion of the elementary excitations can be measured from scattering by a finite-size atomic-trap condensate. As a second example, we point out that a near-resonant scattering experiment can observe quasi-particle creation caused by particle annihilation.

### Neutron star properties in the Thomas-Fermi model

K. Strobel <sup>a,\*</sup>, F. Weber <sup>a,†</sup>, M. K. Weigel <sup>b</sup>,  
and Ch. Schaab <sup>a</sup>

<sup>a</sup> Institut für Theoretische Physik, Universität München

Theresienstrasse 37, D-80333 München, Germany

<sup>b</sup> Sektion Physik, Universität München

Am Coulombwall 1, D-85748 Garching, Germany

May 28, 1997

### Abstract

The modern nucleon-nucleon interaction of Myers and Swiatecki, adjusted to the properties of finite nuclei, the parameters of the mass formula, and the behavior of the optical potential is used to calculate the properties of  $\beta$ -equilibrated neutron star matter, and to study the impact of this equation of state on the properties of (rapidly rotating) neutron stars and their cooling behavior. The results are in excellent agreement with the outcome of calculations performed for a broad collection of sophisticated nonrelativistic as well as relativistic models for the equation of state.

- Advantages of the Thomas-Fermi theory
  - Exact theory for atoms with infinite nuclear charge
  - Simple and elegant model, does not require wavefunctions
  - Naturally includes the exclusion principle and Coulomb repulsion
  - Starting point for the description of electron screening
  - Starting point for more elaborate theories
- Disadvantages
  - Approximations too severe for quantitative (and often qualitative!) agreement with experiment
  - Does not allow interatomic bonds or obtaining information about electronic states



- Extension of the idea proposed by Thomas and Fermi: An  $N$ -electron system has a complex multidimensional wavefunction  $\psi_e$  that depends on the coordinates of all electrons in the system
- Integrating over  $N-1$  degrees of freedom of  $|\psi_e|^2$  will give us the probability of finding one electron in the volume element around  $\vec{r}_1$ , leading us to the electron density

$$n(\vec{r}_1) = N \sum_{\omega_1, \dots, \omega_N} \int |\psi_e(\vec{r}_1 \omega_1, \dots, \vec{r}_N \omega_N)|^2 dr_2 \dots dr_N$$

- Is it possible to formulate an *exact* many-body quantum-mechanical theory completely in terms of  $n(\vec{r})$ ?
- Answer: In principle yes