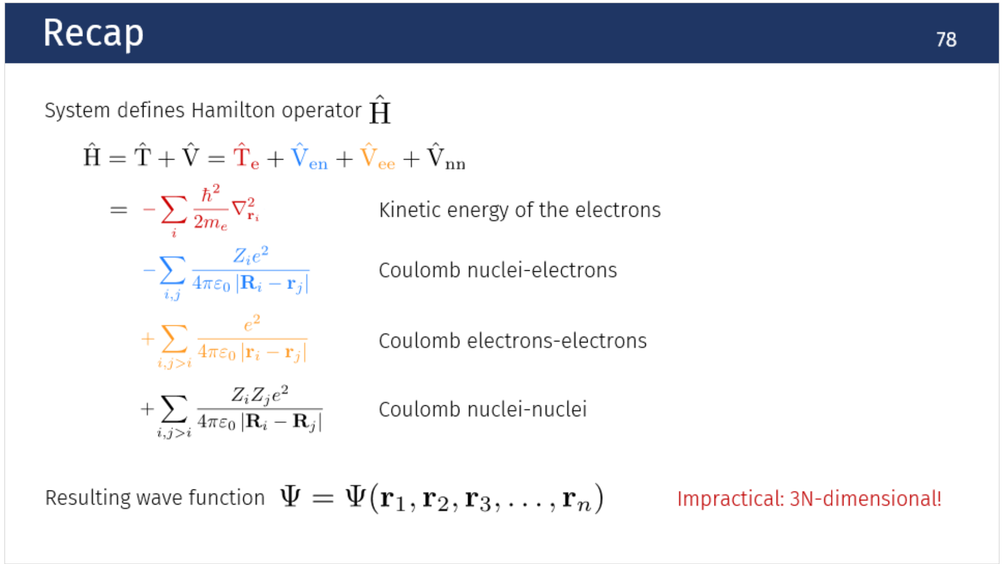
Kohn-Sham Equations

Kohn-Sham equations

Previously:

$$\hat{\mathrm{H}}\,\Psi = E\Psi$$



Recap

78

System defines Hamilton operator $\hat{\mathrm{H}}$

$$\hat{\mathrm{H}} = \hat{\mathrm{T}} + \hat{\mathrm{V}} = \hat{\mathrm{T}}_{\mathrm{e}} + \hat{\mathrm{V}}_{\mathrm{en}} + \hat{\mathrm{V}}_{\mathrm{ee}} + \hat{\mathrm{V}}_{\mathrm{nn}}$$

$= -\sum_{i} \frac{\hbar^2}{2m_e} \nabla^2_{\mathbf{r}_i}$	Kinetic energy of the electrons
$-\sum_{i,j} \frac{Z_i e^2}{4\pi\varepsilon_0 \lvert \mathbf{R}_i - \mathbf{r}_j \rvert}$	Coulomb nuclei-electrons
$+\sum_{i,j>i} \frac{e^2}{4\pi\varepsilon_0 \lvert \mathbf{r}_i - \mathbf{r}_j \rvert}$	Coulomb electrons-electrons
$+\sum_{i,j>i} \frac{Z_i Z_j e^2}{4\pi\varepsilon_0 \lvert \mathbf{R}_i - \mathbf{R}_j \rvert}$	Coulomb nuclei-nuclei

Resulting wave function $\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_n)$ Impractical: 3N-dimensional!

Now:

$$\left[\frac{h^2}{2m_e}\nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{\mathrm{XC}}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

- No summation over i: system of non-interacting electrons of i equations

Terms

$$\left[\frac{h^2}{2m_e}\nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{\mathrm{XC}}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

Kinetic energy
of the electron:
unchanged

Hartree
potential

External
potential

Exchange-Correlation
potential ("everything else"): unknown
nudging electrons towards real density

$$V_H \equiv e^2 \int \frac{\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'$$

circular

Procedure

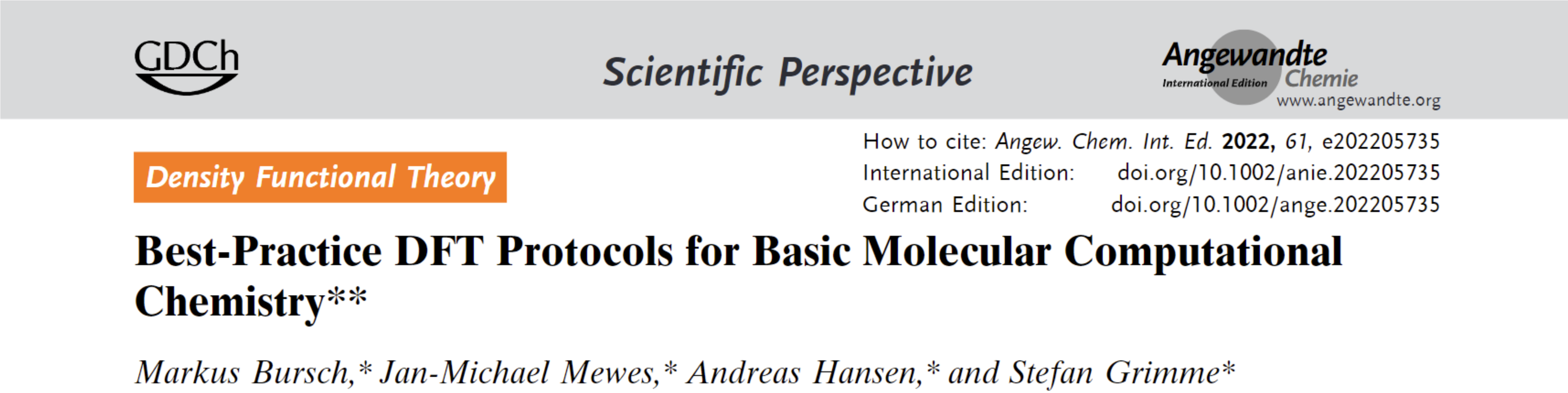
1. Estimate rough electron density (“initial guess”)

2. Solve Kohn-Sham equations using density estimate for single-particle wave functions
3. Calculate electron density from all solutions

4. Repeat 2/3 until the density does not change (by some metric)

- Called self-consistent procedure (“converging”)

Recommendations



Scientific Perspective

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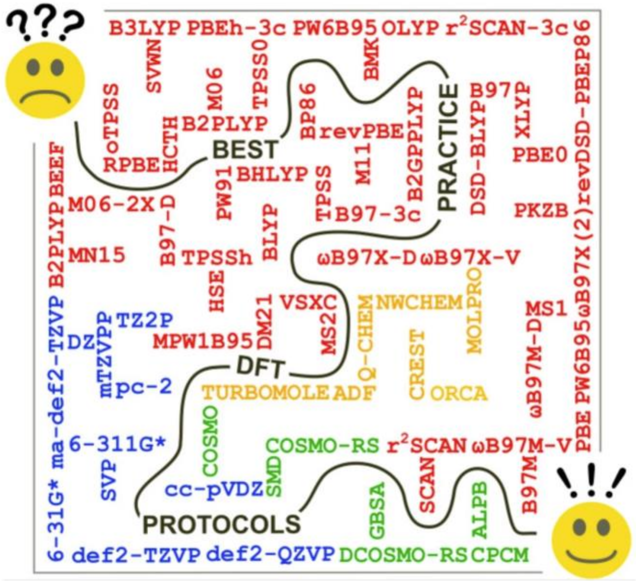
Density Functional Theory

Best-Practice DFT Protocols for Basic Molecular Computational Chemistry**

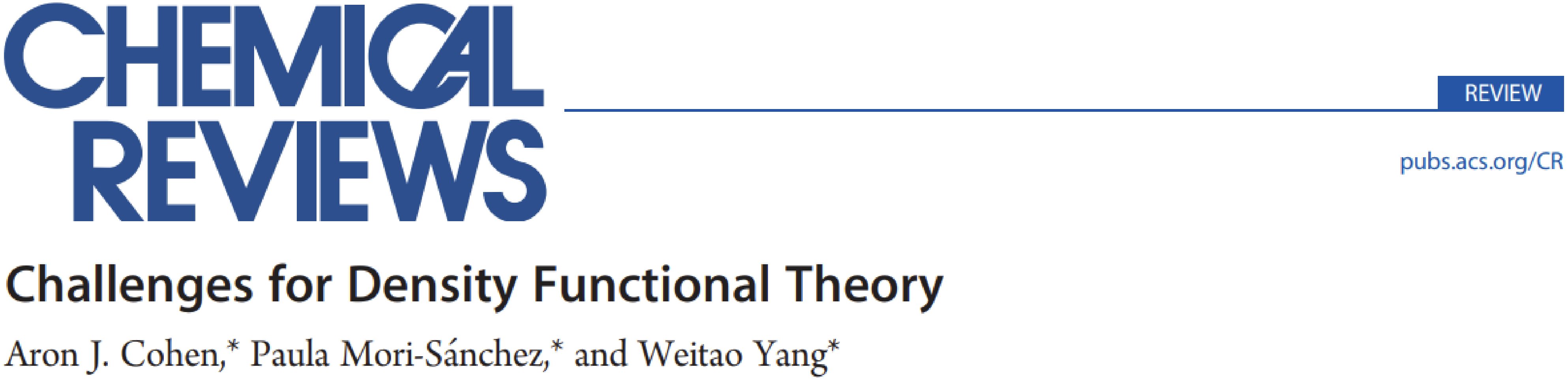
Markus Bursch, Jan-Michael Mewes,* Andreas Hansen,* and Stefan Grimme**



dx.doi.org/10.1002/anie.202205735

Problems

- KS orbital energies have no physical meaning
- Electrons self-interact (so-called self-interaction error, SIE)
  - Orbitals are too delocalized
- No globally reliable functional
- Long-range / Many-body effects
- Dispersion
- Reaction barriers
- Strongly correlated systems: stretched H_2^+



CHEMICAL REVIEWS

REVIEW

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Challenges for Density Functional Theory

Aron J. Cohen,* Paula Mori-Sánchez,* and Weitao Yang*

Hartree-Fock

Hartree-Fock

Mean-field theory to solve the electronic Schrödinger equation

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 - \sum_{A,i}\frac{Z_A}{r_{Ai}} + \sum_{A>B}\frac{Z_A Z_B}{R_{AB}} + \sum_{i>j}\frac{1}{r_{ij}}\right]\Psi(\mathbf{r};\mathbf{R}) = E_{el}\Psi(\mathbf{r};\mathbf{R})$$

$$\left[\hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r};\mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r})\right]\Psi(\mathbf{r};\mathbf{R}) \quad = \quad E_{el}\Psi(\mathbf{r};\mathbf{R})$$

Hartree-Fock

Assuming non-interacting electrons yields Hartree product

$$\Psi_{HP}(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_N) = \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\cdots\chi_N(\mathbf{x}_N)$$

But this approach does not satisfy the antisymmetry principle

$$\chi_1(\mathbf{x}_2)\chi_2(\mathbf{x}_1) = -\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)$$

With a Slater determinant however, it is.

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}$$

Slater determinant:
- Electrons are indistinguishable
- Every electron in every orbital
- Equivalent to mean field treatment
- Satisfies Pauli exclusion

Hartree-Fock

Electronic energy expression

$$E_{el} = \langle \Psi | \hat{H}_{el} | \Psi \rangle$$

$$\hat{H}_{el} = \sum_i h(i) + \sum_{i<j} v(i,j) + V_{NN} \qquad h(i) = -\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}} \qquad v(i,j) = \frac{1}{r_{ij}}$$

Can be cast in integral form

$$E_{HF} = \sum_i \langle i|h|i \rangle + \frac{1}{2}\sum_{ij} [ii|jj] - [ij|ji] \qquad \langle i|h|j \rangle = \int d\mathbf{x}_1 \chi_i^*(\mathbf{x}_1) h(\mathbf{r}_1) \chi_j(\mathbf{x}_1)$$

$$[ij|kl] = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1)\chi_j(\mathbf{x}_1)\frac{1}{r_{12}}\chi_k^*(\mathbf{x}_2)\chi_l(\mathbf{x}_2)$$

Hartree-Fock

Solution

$$h(\mathbf{x}_1)\chi_i(\mathbf{x}_1)+\underbrace{\sum_{j\neq i}\left[\int d\mathbf{x}_2|\chi_j(\mathbf{x}_2)|^2 r_{12}^{-1}\right]\chi_i(\mathbf{x}_1)}_{\text{Coulomb term}}-\underbrace{\sum_{j\neq i}\left[\int d\mathbf{x}_2\chi_j^*(\mathbf{x}_2)\chi_i(\mathbf{x}_2)r_{12}^{-1}\right]\chi_j(\mathbf{x}_1)}_{\text{Exchange term}}=\epsilon_i\chi_i(\mathbf{x}_1)$$

$$\mathcal{J}_j(\mathbf{x}_1)=\int d\mathbf{x}_2|\chi_j(\mathbf{x}_2)|^2 r_{12}^{-1}$$

$$\mathcal{K}_j(\mathbf{x}_1)\chi_i(\mathbf{x}_1)=\left[\int d\mathbf{x}_2\chi_j^*(\mathbf{x}_2)r_{12}^{-1}\chi_i(\mathbf{x}_2)\right]\chi_j(\mathbf{x}_1)$$

Hartree-Fock

Solution

$$\left[h(\mathbf{x}_1) + \sum_{j \neq i} \mathcal{J}_j(\mathbf{x}_1) - \sum_{j \neq i} \mathcal{K}_j(\mathbf{x}_1)\right] \chi_i(\mathbf{x}_1) = \epsilon_i \chi_i(\mathbf{x}_1)$$

$$\left[\mathcal{J}_i(\mathbf{x}_1) - \mathcal{K}_i(\mathbf{x}_1)\right] \chi_i(\mathbf{x}_1) = 0$$

$$\underbrace{\left[h(\mathbf{x}_1) + \sum_{j} \mathcal{J}_j(\mathbf{x}_1) - \mathcal{K}_j(\mathbf{x}_1)\right]}_{\text{Fock operator } f} \chi_i(\mathbf{x}_1) = \epsilon_i \chi_i(\mathbf{x}_1)$$

Solved numerically by optimizing orthonormal orbitals

Hartree-Fock: Roothaan equations

Take

$$\left[h(\mathbf{x}_1) + \sum_j \mathcal{J}_j(\mathbf{x}_1) - \mathcal{K}_j(\mathbf{x}_1)\right]\chi_i(\mathbf{x}_1) = \epsilon_i \chi_i(\mathbf{x}_1)$$

And solve in a basis set

$$\chi_i = \sum_{\mu=1}^{K} C_{\mu i}\tilde{\chi}_\mu$$

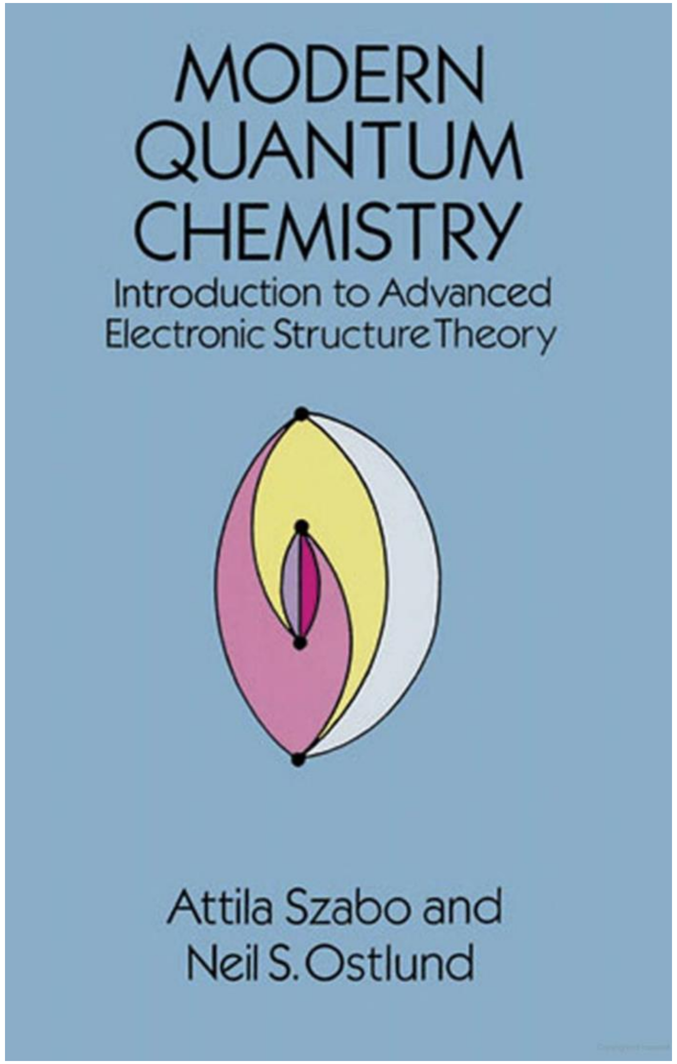
$$f(\mathbf{x}_1)\sum_\nu C_{\nu i}\tilde{\chi}_\nu(\mathbf{x}_1) = \epsilon_i \sum_\nu C_{\nu i}\tilde{\chi}_\nu(\mathbf{x}_1)$$

$$\sum_\nu C_{\nu i}\underbrace{\int d\mathbf{x}_1 \tilde{\chi}^*_\mu(\mathbf{x}_1) f(\mathbf{x}_1)\tilde{\chi}_\nu(\mathbf{x}_1)}_{\text{Fock matrix } F_{\mu\nu}} = \epsilon_i \sum_\nu C_{\nu i}\underbrace{\int d\mathbf{x}_1 \tilde{\chi}^*_\mu(\mathbf{x}_1)\tilde{\chi}_\nu(\mathbf{x}_1)}_{\text{Overlap matrix } S_{\mu\nu}}$$

$$\sum_\nu F_{\mu\nu}C_{\nu i} = \epsilon_i \sum_\nu S_{\mu\nu}C_{\nu i}$$

$$\mathbf{FC} = \mathbf{SC}\epsilon$$

Suggested Literature



MODERN QUANTUM CHEMISTRY

Introduction to Advanced Electronic Structure Theory

Attila Szabo and Neil S. Ostlund