

Kohn-Sham Equations

Previously:

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

Now:

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

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

Recap

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System defines Hamilton operator \hat{H}

$$\begin{aligned} \hat{H} &= \hat{T} + \hat{V} = \hat{T}_e + \hat{V}_{en} + \hat{V}_{ee} + \hat{V}_{nn} \\ &= -\sum_i \frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 && \text{Kinetic energy of the electrons} \\ &\quad -\sum_{i,j} \frac{Z_i e^2}{4\pi\epsilon_0 |\mathbf{R}_i - \mathbf{r}_j|} && \text{Coulomb nuclei-electrons} \\ &\quad +\sum_{i,j>i} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} && \text{Coulomb electrons-electrons} \\ &\quad +\sum_{i,j>i} \frac{Z_i Z_j e^2}{4\pi\epsilon_0 |\mathbf{R}_i - \mathbf{R}_j|} && \text{Coulomb nuclei-nuclei} \end{aligned}$$

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

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

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

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”)

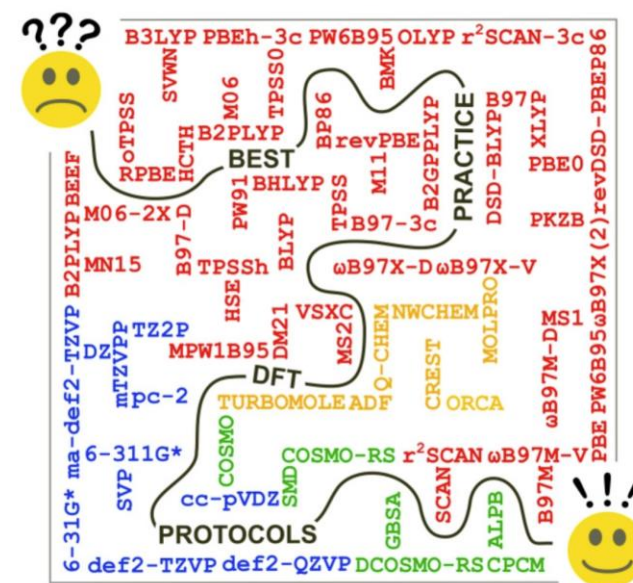


Density Functional Theory

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

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



- 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*