

Density functional theory of atoms and molecules

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Schrodinger's Equation

Electronic hamiltonian in the Born-Oppenheimer approximation

Molecule with N electrons and M nuclei

function of $4N$ variables (3 spatial and 1 spin for each electron)

$$\hat{H}\Psi(\mathbf{r}_1, s_1, \dots, \mathbf{r}_N, s_N) = E\Psi(\mathbf{r}_1, s_1, \dots, \mathbf{r}_N, s_N)$$

$$\hat{H}_{molecule} = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 + \sum_{j>i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{\alpha=1}^M -\frac{Z_\alpha e^2}{|\mathbf{r}_i - \mathbf{R}_\alpha|} \right)$$

Diagram annotations: A red oval encloses the term $\hat{T} + \hat{V}_{ee}$. A red oval encloses the kinetic energy term $-\frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2$ and the electron-electron repulsion term $\sum_{j>i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$. A red oval encloses the nucleus-electron attraction term $\sum_{\alpha=1}^M -\frac{Z_\alpha e^2}{|\mathbf{r}_i - \mathbf{R}_\alpha|}$. A red oval encloses the external potential $v(\mathbf{r}_i)$. Red arrows point from the external potential oval to the nucleus-electron attraction term, and from the $\hat{T} + \hat{V}_{ee}$ oval to the kinetic energy term.

$$P = \sum_{s_i} \int \int \dots \int d\mathbf{r}_1 \dots d\mathbf{r}_N \Psi^*(\mathbf{r}_1, s_1, \dots, \mathbf{r}_N, s_N) \hat{P} \Psi(\mathbf{r}_1, s_1, \dots, \mathbf{r}_N, s_N)$$

Electronic density

function of 3 variables

$$\rho(\mathbf{r}) = \sum_{s_i} \int \int \dots \int d\mathbf{r}_1 \dots d\mathbf{r}_N \Psi^*(\mathbf{r}_1, s_1, \dots, \mathbf{r}_N, s_N) \left[\sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \right] \Psi(\mathbf{r}_1, s_1, \dots, \mathbf{r}_N, s_N)$$

$$= N \sum_{s_i} \int \int \dots \int d\mathbf{r}_2 \dots d\mathbf{r}_N \Psi^*(\mathbf{r}, s_1, \dots, \mathbf{r}_N, s_N) \Psi(\mathbf{r}, s_1, \dots, \mathbf{r}_N, s_N)$$

$$\sum_{s_i} \int \int \dots \int d\mathbf{r}_1 \dots d\mathbf{r}_N \Psi^*(\mathbf{r}_1, s_1, \dots, \mathbf{r}_N, s_N) \Psi(\mathbf{r}_1, s_1, \dots, \mathbf{r}_N, s_N) = 1$$

Normalization $\int d\mathbf{r} \rho(\mathbf{r}) = N$

Local behavior $\rho(\mathbf{r}) \geq 0$

Cusp condition $\left. \frac{\partial \ln \rho_{Sph Av}(r)}{\partial |\mathbf{r} - \mathbf{R}_\alpha|} \right|_{\mathbf{r}=\mathbf{R}_\alpha} = -2Z_\alpha$

Asymptotic behavior $\rho_{Sph Av}(r) \xrightarrow{r \rightarrow \infty} r^\lambda e^{-\gamma r} \quad \gamma = \sqrt{8I}$

Hohenberg-Kohn theorems

Theorem I (Existence)

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \sum_{i=1}^N v(\mathbf{r}_i) = \hat{F} + \sum_{i=1}^N v(\mathbf{r}_i)$$

Wavefunction approach

Given N and $v(\mathbf{r}) \Rightarrow \hat{H} \Rightarrow \Psi(\mathbf{r}_1, s_1, \dots, \mathbf{r}_N, s_N) \Rightarrow$ any property $P \Rightarrow \rho(\mathbf{r})$

Density Functional approach

Given $\rho(\mathbf{r}) \Rightarrow N$ and $v(\mathbf{r}) \Rightarrow \hat{H} \Rightarrow \Psi(\mathbf{r}_1, s_1, \dots, \mathbf{r}_N, s_N) \Rightarrow$ any property P

Total energy as a functional of the electron density

$$E[\rho] = F[\rho] + \int d\mathbf{r} v(\mathbf{r}) \rho(\mathbf{r}) = T[\rho] + V_{ee}[\rho] + \int d\mathbf{r} v(\mathbf{r}) \rho(\mathbf{r})$$

Coulombic

$$T[\rho] = ? \quad V_{ee}[\rho] = J[\rho] + E_x[\rho] + E_c[\rho] \left\{ \begin{array}{l} J[\rho] = \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'| \\ E_x[\rho] = ? \quad \text{Exchange} \\ E_c[\rho] = ? \quad \text{Correlation} \end{array} \right.$$

Kinetic

Hohenberg-Kohn theorems

Theorem II (Variational Principle)

$$E_v[\rho] = F[\rho] + \int d\mathbf{r} v(\mathbf{r})\rho(\mathbf{r}) = T[\rho] + J[\rho] + E_x[\rho] + E_c[\rho] + \int d\mathbf{r} v(\mathbf{r})\rho(\mathbf{r})$$

$$E_0 \leq E_v[\rho]$$

Ground state energy

Energy corresponding to a given electron density

Equality occurs only when the given density is equal to the ground state density

$$\frac{\delta \left(E_v[\rho] - \mu \int d\mathbf{r} \rho(\mathbf{r}) \right)}{\delta \rho(\mathbf{r})} = 0 \quad \Rightarrow \quad \frac{\delta E_v[\rho]}{\delta \rho(\mathbf{r})} = \mu \quad \text{Chemical potential}$$

Three dimensional equation to determine the ground state electron density

$$\Rightarrow \quad \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} + v(\mathbf{r}) = \mu$$

Thomas-Fermi model

$$E_v[\rho] = F[\rho] + \int d\mathbf{r} v(\mathbf{r})\rho(\mathbf{r}) = T[\rho] + J[\rho] + E_x[\rho] + E_c[\rho] + \int d\mathbf{r} v(\mathbf{r})\rho(\mathbf{r})$$

Approximate the kinetic energy by the one corresponding to a free electron gas using the local density approximation (LDA)

$$T[\rho] \approx \frac{3}{10} (3\pi^2)^{2/3} \int d\mathbf{r} \rho(\mathbf{r})^{5/3}$$

Approximate the electron-electron interaction by the Coulomb repulsion energy, neglect the exchange and correlation contributions.

$$J[\rho] = \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad E_x[\rho] \approx 0 \quad E_c[\rho] \approx 0$$

Thomas-Fermi energy functional for an atom

$$E_v^{TF}[\rho] = \frac{3}{10} (3\pi^2)^{2/3} \int d\mathbf{r} \rho(\mathbf{r})^{5/3} + \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - Z \int d\mathbf{r} \frac{\rho(\mathbf{r})}{r}$$

Thomas-Fermi model

The minimization of the energy leads to an equation for the electron density whose solution has the following features:

For neutral atoms

- No shell structure
- Behavior near the nucleus (diverges) $\longrightarrow \rho(\mathbf{r}) \xrightarrow{r \rightarrow 0} r^{-3/2}$
- Asymptotic behavior (infinite size) $\longrightarrow \rho(\mathbf{r}) \xrightarrow{r \rightarrow \infty} r^{-6}$
- Total energy is $\longrightarrow E = -0.7687 Z^{7/3}$

Cations have finite size

Anions does not exist

Thomas-Fermi is exact for neutral atoms ($N=Z$) when $Z \rightarrow \infty$

Atoms do not bind to form molecules

Kohn-Sham theory

Independent electron system whose density reproduces the ground state density of the interacting N electron system

$$E_{KS}[\rho] = T_S[\rho] + J[\rho] + E_{XC}[\rho] + \int d\mathbf{r} v(\mathbf{r})\rho(\mathbf{r})$$

$$T_S[\rho] = \sum_i^{occ} n_i \int d\mathbf{r} \phi_i^{KS}(\mathbf{r})^* \left\{ -\frac{1}{2} \nabla^2 \right\} \phi_i^{KS}(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_i^{occ} n_i \phi_i^{KS}(\mathbf{r})^* \phi_i^{KS}(\mathbf{r})$$

$$E_{XC}[\rho] = E_X[\rho] + E_C[\rho]$$

Minimization of the Kohn-Sham energy with respect to the set of orbitals

$$\left[-\frac{1}{2} \nabla^2 + v(\mathbf{r}) + v_{Coul}(\mathbf{r}) + v_{XC}(\mathbf{r}) \right] \phi_i^{KS}(\mathbf{r}) = \varepsilon_i^{KS} \phi_i^{KS}(\mathbf{r})$$

$$v_{Coul}(\mathbf{r}) = \frac{\delta J[\rho]}{\delta \rho(\mathbf{r})} \quad v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}$$

Approximate Kohn-Sham (KS) and Hartree-Fock (HF)

- KS is a $4N$ dimensional problem
- KS wavefunction is given by a single determinant that leads to the exact ground-state electron density
- It includes correlation in a very simple way, in comparison with post Hartree-Fock wavefunction methods
- Computational effort similar to Hartree-Fock
- The exact form of the exchange-correlation energy functional is unknown

Some important properties of the exact Ex

First order reduced density matrix

$$\gamma(\mathbf{r}, \mathbf{r} + \mathbf{R}) = \sum_i^{\text{occ}} n_i \phi_i(\mathbf{r} + \mathbf{R})^* \phi_i(\mathbf{r})$$

Exchange energy

$$E_X[\rho] = \int d\mathbf{r} e_X[\rho](\mathbf{r}) \quad \rho_X(\mathbf{r}, \mathbf{r} + \mathbf{R}) = -\frac{1}{2} |\gamma(\mathbf{r}, \mathbf{r} + \mathbf{R})|^2 / \rho(\mathbf{r})$$

$$e_X[\rho](\mathbf{r}) = \frac{1}{2} \rho(\mathbf{r}) \int d\mathbf{R} \rho_X(\mathbf{r}, \mathbf{r} + \mathbf{R}) / R$$

Properties

$$\rho_X(\mathbf{r}, \mathbf{r}) = -\rho(\mathbf{r}) / 2$$

$$\rho_X(\mathbf{r}, \mathbf{r} + \mathbf{R}) \leq 0$$

$$\int d\mathbf{R} \rho_X(\mathbf{r}, \mathbf{r} + \mathbf{R}) = -1$$

$$E_X[\rho] \geq -1.679 \int d\mathbf{r} \rho^{4/3}(\mathbf{r})$$

-1.092

Some important properties of the exchange potential

Asymptotic behavior

$$v_X[\rho; \mathbf{r}] = \frac{\delta E_X[\rho]}{\delta \rho(\mathbf{r})} \quad v_X[\rho; \mathbf{r}] \xrightarrow{r \rightarrow \infty} -\frac{1}{r}$$

Derivative discontinuity

$$v_X^+(\mathbf{r}) \Big|_{N_0+\delta} - v_X^-(\mathbf{r}) \Big|_{N_0-\delta} = \Delta_X$$

N_0 is an integer

Local Density Approximation (LDA) to Exc

Approximate the exchange energy by the one corresponding to a free electron gas using the local density approximation (LDA)-Dirac Exchange

$$E_X^D[\rho] \approx -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int d\mathbf{r} \rho(\mathbf{r})^{4/3}$$

Approximate the correlation energy by the one corresponding to a free electron gas using the local density approximation (LDA)-Wigner correlation

$$E_C^W[\rho] \approx -\int d\mathbf{r} \frac{\rho(\mathbf{r})}{17.7 + 2.27\rho(\mathbf{r})^{-1/3}}$$

Actually the most used LDA correlation is VWN

Dirac, P. A. M. Proc. Cambridge Phil. Soc. 1930, 26, 376.

Wigner, E. Phys. Rev. 1934, 46, 1002.

Vosko S. H., Wilk L., Nusair M. Can. J. Phys. 1980, 58, 1200.

Gradient Expansion Approximation (GEA)

In order to take into account the non-uniformity one can make an expansion in terms of the gradient of the electronic density

$$E_X^{GEA}[\rho] \approx -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int d\mathbf{r} \rho(\mathbf{r})^{4/3} - \frac{5}{648\pi} \left(\frac{3}{\pi} \right)^{2/3} \int d\mathbf{r} \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})^{4/3}} + \dots$$

Functional derivative

$$v_X^{LDA}(\mathbf{r}) = \frac{\delta E_X[\rho]}{\delta\rho(\mathbf{r})} \xrightarrow{r \rightarrow \infty} -e^{-4\gamma r/3}$$

$$v_X^{GEA}(\mathbf{r}) = \frac{\delta E_X[\rho]}{\delta\rho(\mathbf{r})} \xrightarrow{r \rightarrow \infty} -\infty$$

Generalized Gradient Approximation (GGA) to Exc





Impose the positivity constraint and the sum rule by introducing real space cutoffs

$$\begin{aligned} \rho_X(\mathbf{r}, \mathbf{r} + \mathbf{R}) &\leq 0 \\ \int d\mathbf{R} \rho_X(\mathbf{r}, \mathbf{r} + \mathbf{R}) &= -1 \end{aligned} \quad E_X^{GGA}[\rho] \approx -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int d\mathbf{r} \rho(\mathbf{r})^{4/3} F_X(s)$$

Reduced density gradient

$$S = \frac{|\nabla\rho(\mathbf{r})|}{2 k_F(\mathbf{r}) \rho(\mathbf{r})} \quad k_F(\mathbf{r}) = (3\pi^2 \rho(\mathbf{r}))^{1/3}$$
$$v_X^{GGA}(\mathbf{r}) = \frac{\delta E_X[\rho]}{\delta\rho(\mathbf{r})} \xrightarrow{r \rightarrow \infty} \begin{cases} -1/r \\ -e^{-\delta r} \end{cases}$$

Aspects to be considered in the design of F_X

- Behavior at small s  $F_X(s) \xrightarrow{s \rightarrow 0} 1 + \mu s^2$
- $0 \leq s \leq 3$  Physically important region for the energy
- Behavior at large s ($s \rightarrow \infty$)  Important for the exchange potential (eigenvalues and orbitals)
- Derivative discontinuity  Important for the exchange potential (eigenvalue of the HOMO)

Non-empirical GGA's

PBE

$$F_X^{PBE}(s) = 1 + \kappa - \frac{\kappa}{1 + \frac{\mu s^2}{\kappa}} \quad v_X^{PBE}(\mathbf{r}) = \frac{\delta E_X[\rho]}{\delta \rho(\mathbf{r})} \xrightarrow{r \rightarrow \infty} -e^{-\delta r}$$

NCAP

$$F_X^{NCAP}(s) = 1 + \mu \tanh(s) \sinh^{-1}(s) \frac{1 + \alpha((1 - \zeta) s \ln(1 + s) + \zeta s)}{1 + \beta \tanh(s) \sinh^{-1}(s)}$$

$$v_X^{GGA}(\mathbf{r}) = \frac{\delta E_X[\rho]}{\delta \rho(\mathbf{r})} \xrightarrow{r \rightarrow \infty} -c/r$$

J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996)

Carmona-Espindola, J. L. Gázquez, A. Vela, and S. B. Trickey, J. Chem. Theory Comput. 15, 303 (2019)

J. P. Perdew, Phys. Rev. B 33, 8822 (1986)

Jacob's ladder

- Accuracy is expected to increase climbing the ladder.
- Computational effort increases when climbing the ladder.
- Precision at each step may be increased.

Meta-GGA

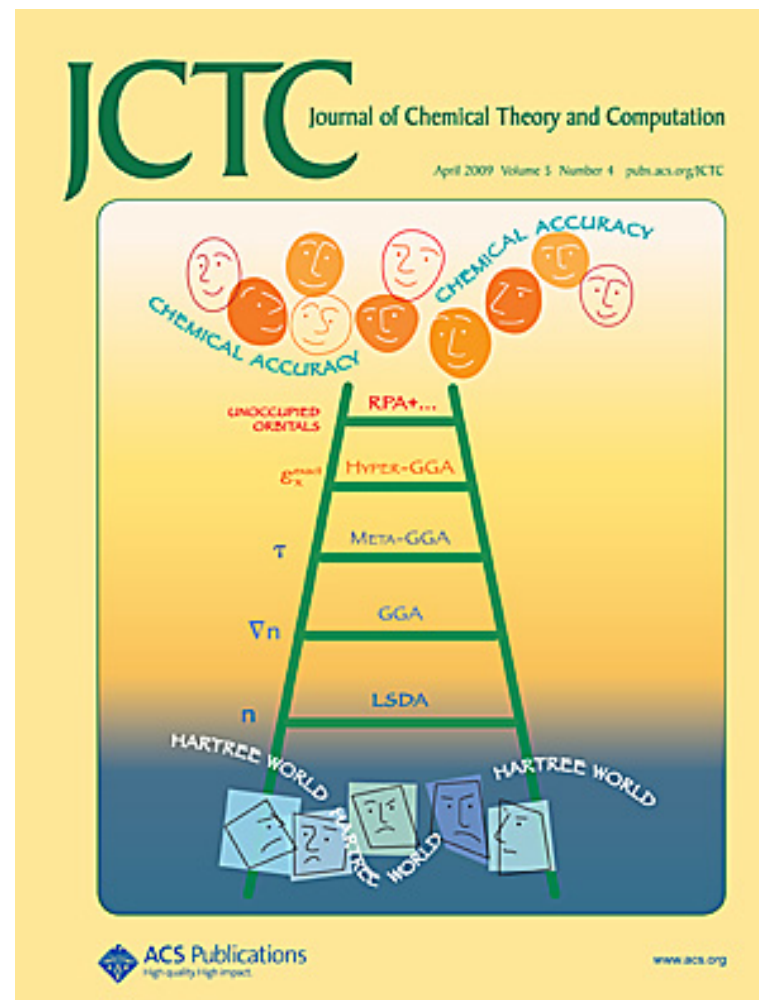
$$\tau(\mathbf{r}) = \frac{1}{2} \sum_i^{occ} n_i |\nabla \phi_i^{KS}(\mathbf{r})|^2$$

Hyper-GGA (Global and Local Hybrids)

$$E_X[\{\phi_i\}] = -\frac{1}{2} \sum_{i=1}^{occ} \sum_{j=1}^{occ} \iint d\mathbf{r} d\mathbf{r}' \phi_i^*(\mathbf{r}) \phi_j^*(\mathbf{r}') \phi_i(\mathbf{r}') \phi_j(\mathbf{r}) / |\mathbf{r} - \mathbf{r}'|$$

RPA (Unoccupied orbitals)

Perdew, J. P.; Schmidt, K. in *Density Functional Theory and its Application to Materials*; Van Doren, V. E., Van Alsenoy, C., Geerlings, P., Eds.; AIP, Melville: New York, 2001; pp 1.



Exchange and correlation energies

MAD for the exchange, correlation and exchange-correlation energies of the noble gas atoms Ne, Ar, Kr, Xe in Hartrees

	E_X	E_C	E_{XC}
LDA	4.35	1.17	3.18
PBE	0.41	0.06	0.46
CAP	0.98	0.06	1.04
NCAP	0.20	0.14	0.07
SCAN	0.14	0.07	0.08
B3LYP	0.38	0.27	0.11
CAM-B3LYP	0.17	0.16	0.02

Energy differences, Bond distances and Dipole moments

MAD for the heats of formation of the G3 set in kcal/mol (223 molecules), barrier heights of the BH76 set of reactions in kcal/mol, binding energy of weakly bonded systems of the WB31 set in kcal/mol, bond distances of the T-96R set in Å and dipole moments of the Hait and Head-Gordon set in Debyes (144 molecules)

	G3	BH	WB	BD	DM
LDA	118.3	15.5	3.6	0.082	0.159
PBE	21.2	9.9	1.6	0.018	0.153
CAP	9.2	7.6	2.7	0.022	0.141
NCAP	6.0	8.0	2.4	0.025	0.143
SCAN	5.1	8.6	1.6	0.009	0.089
B3LYP	5.7	5.9	1.2	0.011	0.075
CAM-B3LYP	3.2	3.7	1.0	0.014	0.067

Ionization potential theorem

Comparison of the HOMO eigenvalue with the experimental ionization potential (IP) in eV for some of the noble gases. The values for NCAP correspond to the shifted exchange potential.

	Ne	Ar	Kr	Xe	MAD
LDA	13.56	10.40	9.42	8.42	5.41
PBE	13.35	10.29	9.28	8.28	5.57
CAP	13.11	10.13	9.15	8.17	5.73
NCAP	21.19	17.44	16.19	14.92	1.76
SCAN	14.00	10.73	9.69	8.62	5.11
B3LYP	15.65	11.67	10.47	9.28	4.10
CAM-B3LYP	17.67	13.48	12.19	10.89	2.31
Hartree-Fock	23.14	16.08	14.26	12.44	0.62
Exp. IP	21.57	15.76	14.00	12.13	

Excited states (TDDFT)

MAD for 17 valence and 23 Rydberg excitation energies in eV for a test set with four molecules. The values for NCAP correspond to the unshifted exchange potential

	Valence	Rydberg	Total
LDA	0.30	1.29	0.87
PBE	0.35	1.47	1.00
CAP	0.32	1.25	0.86
NCAP	0.26	0.64	0.48
B3LYP	0.40	0.88	0.68
CAM-B3LYP	0.42	0.46	0.44

Molecules considered: N₂ (8 v, 2 R), CO (4 v, 6 R), CH₂O (3 v, 7 R) and C₂H₄ (2 v, 8 R)

Hartree-Fock theory

Best single determinant wavefunction

$$E_{HF}[\{\phi_i^{HF}\}] = T_S[\{\phi_i^{HF}\}] + J[\{\phi_i^{HF}\}] + E_X^{HF}[\{\phi_i^{HF}\}] + \int d\mathbf{r} v(\mathbf{r})\rho(\mathbf{r})$$

$$T_S[\{\phi_i^{HF}\}] = \sum_i^{occ} n_i \int d\mathbf{r} \phi_i^{HF}(\mathbf{r})^* \left\{ -\frac{1}{2} \nabla^2 \right\} \phi_i^{HF}(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_i^{occ} n_i \phi_i^{HF}(\mathbf{r})^* \phi_i^{HF}(\mathbf{r})$$

$$J[\{\phi_i^{HF}\}] = \frac{1}{2} \sum_{i=1}^{occ} \sum_{j=1}^{occ} \iint d\mathbf{r} d\mathbf{r}' \phi_i^{*HF}(\mathbf{r}) \phi_j^{*HF}(\mathbf{r}') \phi_i^{*HF}(\mathbf{r}) \phi_j^{*HF}(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|$$

$$E_X^{HF}[\{\phi_i^{HF}\}] = -\frac{1}{2} \sum_{i=1}^{occ} \sum_{j=1}^{occ} \iint d\mathbf{r} d\mathbf{r}' \phi_i^{*HF}(\mathbf{r}) \phi_j^{*HF}(\mathbf{r}') \phi_i^{*HF}(\mathbf{r}') \phi_j^{*HF}(\mathbf{r}) / |\mathbf{r} - \mathbf{r}'|$$

Minimization of the Hartree-Fock energy with respect to the set of orbitals

$$\left[-\frac{1}{2} \nabla^2 + v(\mathbf{r}) + v_{Coul}^{HF}(\mathbf{r}) + v_X^{HF}(\mathbf{r}) \right] \phi_i^{HF}(\mathbf{r}) = \varepsilon_i^{HF} \phi_i^{HF}(\mathbf{r})$$

Approximate Kohn-Sham (KS) and Hartree-Fock (HF)

- HF and KS are $4N$ dimensional problems
- HF Best single determinant wavefunction
- KS wavefunction is given by a single determinant that leads to the exact ground-state electron density
- Computational effort for both is similar
- HF does not include the correlation effects while KS does
- HF cancels correctly the self-interaction while Approximate KS does not

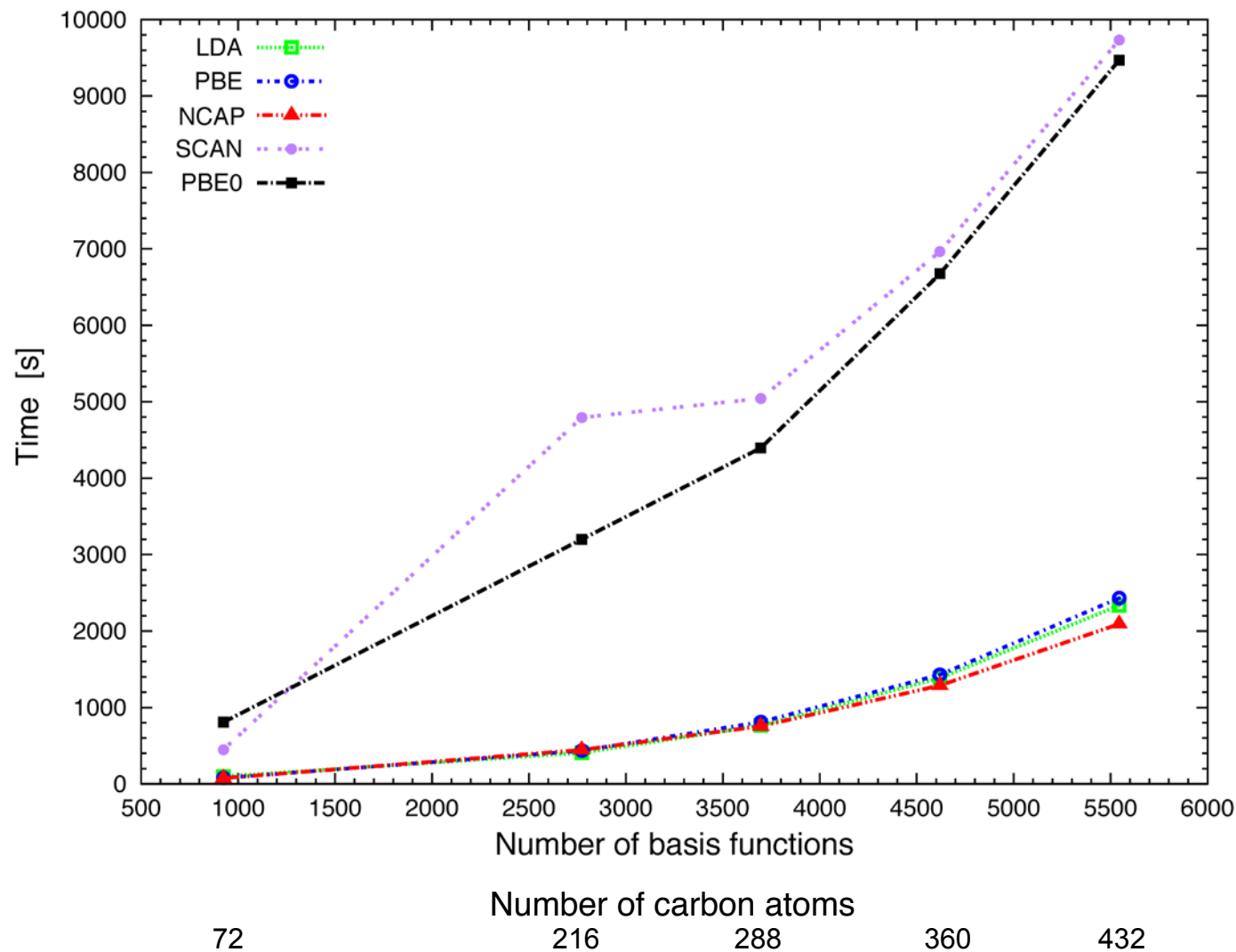
Escalamiento y errores promedio

Métodos	Escalamiento	Errores promedio en kcal/mol
Hartree-Fock	N^4	> 10.0
Kohn-Sham	N^4	1.0-5.0
MP2	N^5	10.4
MP3, CISD (Excitaciones simples y dobles)	N^6	1.7-5.8
MP4	N^7	0.3-1.3
MP5, CISDT (Excitaciones simples, dobles y triples)	N^8	0.8
MP6	N^9	0.3
MP7, CISDTQ (Excitaciones simples, dobles, triples y cuádruples)	N^{10}	0.01

Moléculas HB, H₂O y HF

Computer effort for several functionals in deMon2k

Carbon nanotubes



Final remarks

- The Kohn-Sham approach of density functional theory has become a very powerful tool to perform electronic structure calculations.
- May be used to determine the electronic structure of small, medium and large systems.
- May be applied to a wide variety of Chemical species.
- It has become a very valuable complement to experimental research.