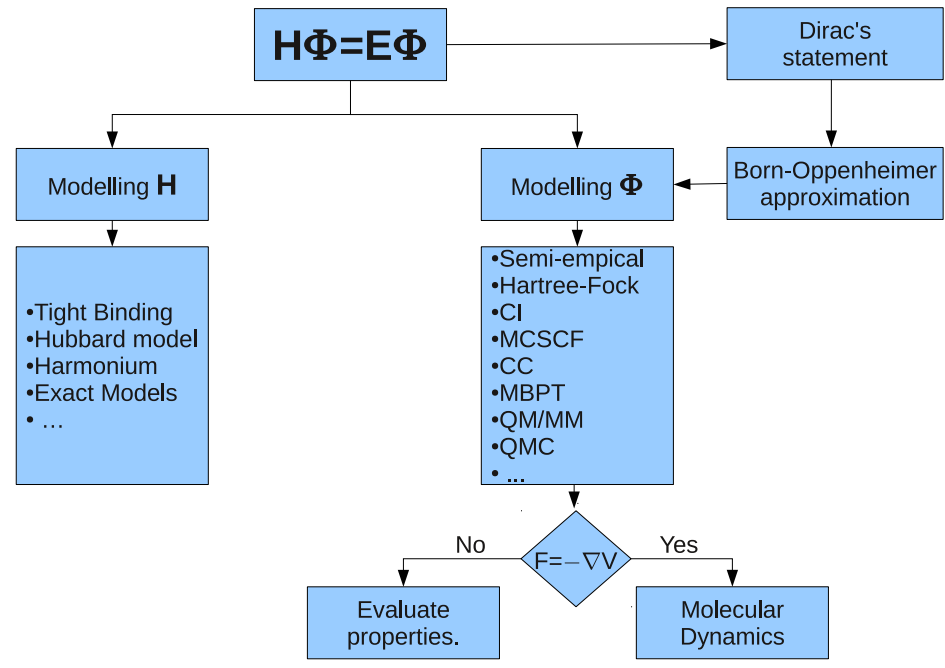


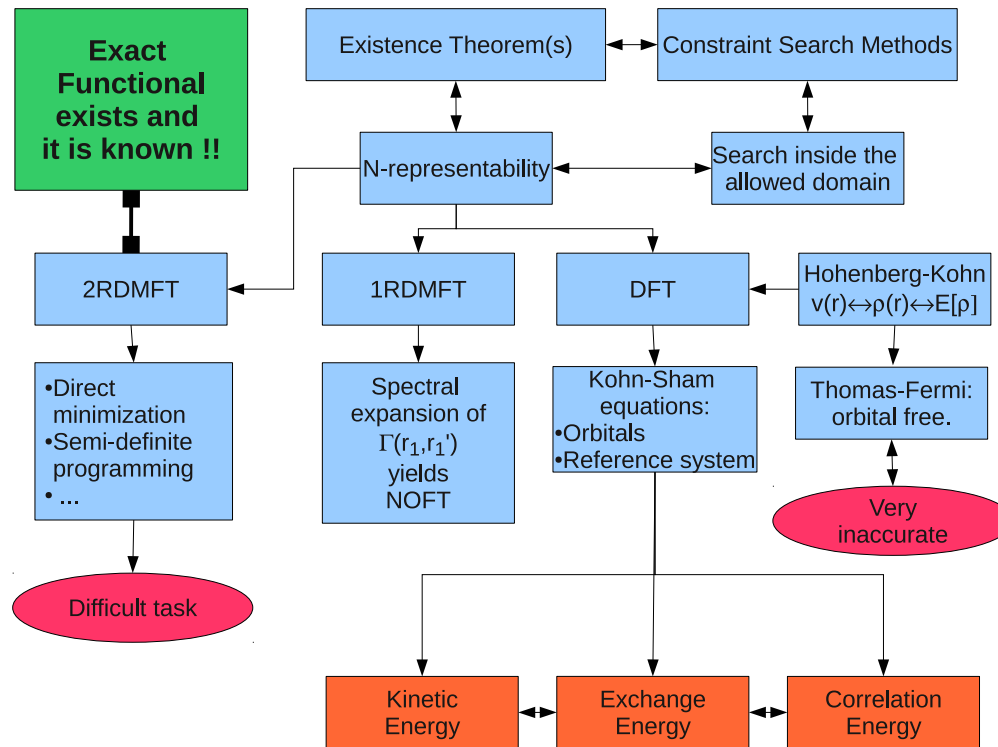
# Quantum Mechanical Methods for the Elucidation of the (Molecular) Electronic Structure.

**Jesus M. Ugalde**

Kimika Fakultatea, Euskal Herriko Unibertsitatea and Donostia  
International Physics Center (DIPC); P.K. 1072, 20080 Donostia,  
Euskadi (Spain)

<http://www.ehu.es/chemistry/theory>





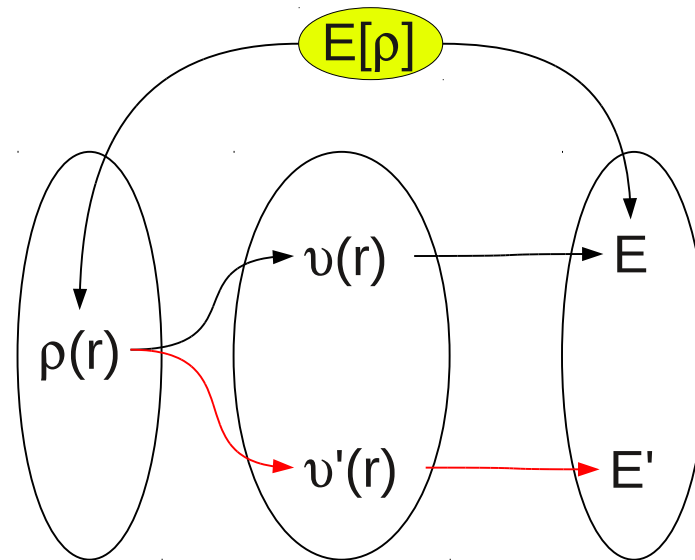
# Introduction to DFT like Electronic Structure Methods.

**Jesus M. Ugalde**

Kimika Fakultatea, Euskal Herriko Unibertsitatea, and Donostia  
International Physics Center (DIPC); P.K. 1072, 20080 Donostia,  
Euskadi (Spain)

<http://www.ehu.es/chemistry/theory>

# The Hohenberg-Kohn Theorem



# The Hohenberg-Kohn Theorem

Let the ground states of  $\hat{H}$  and  $\hat{H}'$  be nondegenerate,

$$\begin{aligned} E' &= \langle \Psi' | \hat{H}' | \Psi' \rangle < \langle \Psi | \hat{H}' | \Psi \rangle = \langle \Psi | \hat{H} + \hat{V}' - \hat{V} | \Psi \rangle \\ &= E + \int d\mathbf{r} [v'(\mathbf{r}) - v(\mathbf{r})] \rho(\mathbf{r}) \end{aligned}$$

Alternatively,

$$\begin{aligned} E &= \langle \Psi | \hat{H} | \Psi \rangle < \langle \Psi' | \hat{H} | \Psi' \rangle = \langle \Psi' | \hat{H}' + \hat{V} - \hat{V}' | \Psi' \rangle \\ &= E' + \int d\mathbf{r} [v(\mathbf{r}) - v'(\mathbf{r})] \rho(\mathbf{r}) \end{aligned}$$

where in the last line we have used the assumption that

$$\langle \Psi' | \hat{\rho} | \Psi' \rangle = \rho(\mathbf{r}) = \langle \Psi | \hat{\rho} | \Psi \rangle$$

Adding the two inequalities we obtain

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

The Hohenberg–Kohn theorem shows that the electron density uniquely determines the external potential. But the external potential uniquely determines the wave function, through the Schrödinger equation. Thus, the electron density uniquely determines the wave function, *i.e.*:  $\Psi$  can be seen as a functional of  $\rho$ .

# The Energy Variational Principle

Let us define:

$$F[\rho] = \langle \Psi[\rho] | [\hat{T} + \hat{U}] | \Psi[\rho] \rangle = T[\rho] + U[\rho]$$

As shown above, the energy can be expressed as

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

Now consider another electron-density  $\rho'(\mathbf{r}) \neq \rho(\mathbf{r})$ , associated through the above demonstrated one-to-one relationship with another external potential  $v'$ . Then:

$$\begin{aligned} E[\rho'] &= F[\rho'] + \int d\mathbf{r} \rho'(\mathbf{r}) v(\mathbf{r}) \quad [\text{Since } \rho' \text{ is } N - \text{representable}] \\ &= \langle \Psi'[\rho'] | [\hat{T} + \hat{U} + \hat{V}] | \Psi'[\rho'] \rangle > \langle \Psi[\rho] | [\hat{T} + \hat{U} + \hat{V}] | \Psi[\rho] \rangle = E[\rho] \end{aligned}$$

The functional  $E_v[\rho]$  achieves its minimum value for the true ground state electron density associated with the external potential  $v$ .



# The Euler Equation of DFT

Variational functional:

$$\Omega = E[\rho] - \mu \left( \int d\mathbf{r} \rho(\mathbf{r}) - N \right)$$

Euler equation:

$$\frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} - \mu = 0$$

# The Chemical Potential: $\mu$

$$E [N, \rho(\mathbf{r})] \rightarrow E [N, v(\mathbf{r})]$$

$$dE = \left( \frac{\partial E}{\partial N} \right)_v dN + \int \left( \frac{\delta E}{\delta v(\mathbf{r})} \right)_\rho \delta v(\mathbf{r}) d\mathbf{r}$$

Use

$$\int d\mathbf{r} \delta \rho(\mathbf{r}) = dN ; \mu = \left( \frac{\partial E}{\partial N} \right)_v ; \left( \frac{\delta E}{\delta v(\mathbf{r})} \right)_\rho = \rho(\mathbf{r})$$

to obtain the fundamental equation for the chemical reactivity:

$$dE = \mu dN + \int \rho(\mathbf{r}) \delta v(\mathbf{r}) d\mathbf{r}$$

Which is the entry point to "Conceptual DFT".

# The Kohn-Sham formulation

Recall the Euler equation:

$$\frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} - \mu = 0 ; E[\rho] = T[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) v(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \mathcal{E}_{xc}[\rho]$$

**Theorem. (Gilbert, Phys. Rev. B 12, 2111 (1975))**

$$\forall \rho(\mathbf{r}) \in \{N - repr\}, \exists \left\{ (\psi_i)_{i=1}^N / \langle \psi_i | \psi_j \rangle = \delta_{ij} \right\} / \rho(\mathbf{r}) = \sum_{i=1}^N \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r})$$

Consider the non-interacting system described by the single Slater determinant made by the  $\{\psi_i\}_{i=1}^N$  orbitals and estimate its kinetic energy\*, namely:

$$T_s = \sum_{i=1}^N \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle$$

and express the energy of the real system as:

$$E[\rho] = T_s[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int d\mathbf{r}d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho]$$

$$E_{xc}[\rho] = \mathcal{E}_{xc}[\rho] + (T[\rho] - T_s[\rho])$$

- **The exchange-correlation functional contains some undetermined kinetic energy**

\*Its non-interacting potential will be determined later

The new expression for the Euler equation is:

$$\frac{\delta T_s [\rho]}{\delta \rho(\mathbf{r})} + \underbrace{v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}}_{v_{eff}(\mathbf{r})} + \frac{\delta E_{xc} [\rho]}{\delta \rho(\mathbf{r})} = \mu$$

Once  $E_{xc} [\rho]$  is determined, we can write an explicit expression for the potential of the non-interacting system and complete the Kohn-Sham equations:

$$\left[ -\frac{1}{2} \nabla_i^2 + v_{eff}(\mathbf{r}) \right] \psi_i = \epsilon_i \psi_i; \quad i = 1, N$$

# The Kohn-Sham Implementation

1. Devise:  $E_{xc}[\rho] \rightarrow v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}$

2. Make a guess for the Kohn-Sham orbitals  $\{\psi_i\}_{i=1}^N$

- Build:  $v_{eff}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} + v_{xc}(\mathbf{r})$

- Solve:  $\left[-\frac{1}{2}\nabla_i^2 + v_{eff}(\mathbf{r})\right] \psi_i = \epsilon_i \psi_i, i = 1, N$  ; **until consistency**

3. Calculate:  $E[\rho] = T_s[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int d\mathbf{r}d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[\rho]$

# The exchange–correlation functional

$$E_{ee} = \int d\mathbf{r}d\mathbf{r}' \frac{\Gamma_2(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

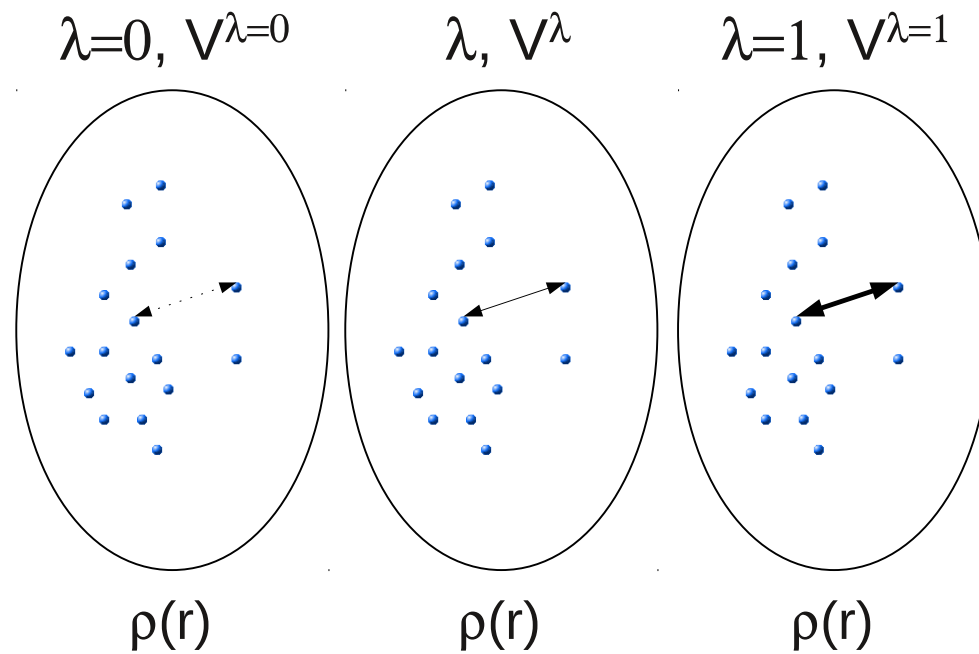
$$\Gamma_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{2} \int |\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_3 \dots d\mathbf{r}_N$$

$$\Gamma_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} \rho(\mathbf{r}_1) [\rho(\mathbf{r}_2) + \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2)]$$

$$E_{ee}[\rho] = \frac{1}{2} \int d\mathbf{r}d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{1}{2} \int d\mathbf{r}d\mathbf{r}' \frac{\rho(\mathbf{r})\rho_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = J[\rho] + \frac{\mathcal{E}_{xc}[\rho]}{[E_{xc}[\rho] - (T[\rho] - T_s[\rho])]}$$

# The Adiabatic Connection

$$\hat{H}^\lambda = \hat{T} + \hat{V}^\lambda + \lambda \hat{U}, 0 \leq \lambda \leq 1$$





$$\hat{H}^\lambda = \hat{T} + \hat{V}^\lambda + \lambda \hat{U}, 0 \leq \lambda \leq 1$$

$$\hat{V}^\lambda / \langle \Psi^\lambda | \hat{\rho} | \Psi^\lambda \rangle = \rho(\mathbf{r}), \forall \lambda. \text{ Hence : } \hat{V}^{\lambda=0} = v_{eff}(\mathbf{r}), \hat{V}^{\lambda=1} = v(\mathbf{r})$$

$$\int_0^1 \left( \frac{\partial E_\lambda}{\partial \lambda} \right) d\lambda = E_{\lambda=1} - E_{\lambda=0}$$

$$d\hat{H}^\lambda = \left( \frac{\partial \hat{H}^\lambda}{\partial \lambda} \right) d\lambda = \left( \frac{\partial V^\lambda}{\partial \lambda} \right) d\lambda + \hat{U} d\lambda$$

$$\left( \frac{\partial E_\lambda}{\partial \lambda} \right) d\lambda = \int d\mathbf{r} \rho(\mathbf{r}) \left( \frac{\partial V^\lambda}{\partial \lambda} \right) d\lambda + \frac{1}{2} d\lambda J[\rho] + \frac{1}{2} d\lambda \int \frac{\rho(\mathbf{r}_1) \rho_{xc}^\lambda(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

$$E_{\lambda=1} - E_{\lambda=0} = \int d\mathbf{r} \rho(\mathbf{r}) \int_0^1 \left( \frac{\partial V^\lambda}{\partial \lambda} \right) d\lambda + \frac{1}{2} J[\rho] + \frac{1}{2} \int \frac{\rho(\mathbf{r}_1) \int_0^1 \rho_{xc}^\lambda(\mathbf{r}_1, \mathbf{r}_2) d\lambda}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

$$E_{\lambda=0} = T_S + \int d\mathbf{r} \rho(\mathbf{r}) V^{\lambda=0}$$

$$E_{\lambda=1} = T_S + \int d\mathbf{r} \rho(\mathbf{r}) V^{\lambda=1} + \frac{1}{2} J[\rho] + \int \frac{\rho(\mathbf{r}_1) \tilde{\rho}_{xc}(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

$$E = T + \int d\mathbf{r} \rho(\mathbf{r}) V^{\lambda=1} + \frac{1}{2} J[\rho] + \int \frac{\rho(\mathbf{r}_1) \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

Same expressions upon consideration of the following equivalencies:

$$T_S \leftrightarrow \tilde{\rho}_{xc}(\mathbf{r}_1, \mathbf{r}_2) = \int_0^1 \rho_{xc}^\lambda(\mathbf{r}_1, \mathbf{r}_2) d\lambda$$
$$T \leftrightarrow \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2)$$

The adiabatic connection has adsorbed the excess kinetic energy term into an exchange–correlation hole description.

# The Local Density Approximation

---

$$E_{xc}[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) \times \varepsilon_{xc}[\rho(\mathbf{r})] d\mathbf{r}$$

$$\varepsilon_{xc}[\rho(\mathbf{r}_1)] = \frac{1}{2} \int \frac{\int_0^1 \rho_{xc}^\lambda(\mathbf{r}_1, \mathbf{r}_2) d\lambda}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2$$

$$\varepsilon_{xc}[\rho(\mathbf{r})] = \varepsilon_x[\rho(\mathbf{r})] + \varepsilon_c[\rho(\mathbf{r})]$$

$$\varepsilon_x^{LDA}[\rho] = -\frac{3}{4} \left( \frac{3\rho(\mathbf{r})}{\pi} \right)^{1/3}$$

$$\varepsilon_c^{VWN}[\rho] = \mathcal{F}[\rho]$$

## Practical Approximate Exchange-Correlation Functionals

$$E_{xc} = \int d\mathbf{r} \rho(\mathbf{r}) \varepsilon_{xc}(\rho^\alpha, \rho^\beta, \nabla\rho^\alpha, \nabla\rho^\beta, \tau^\alpha, \tau^\beta, \dots)$$

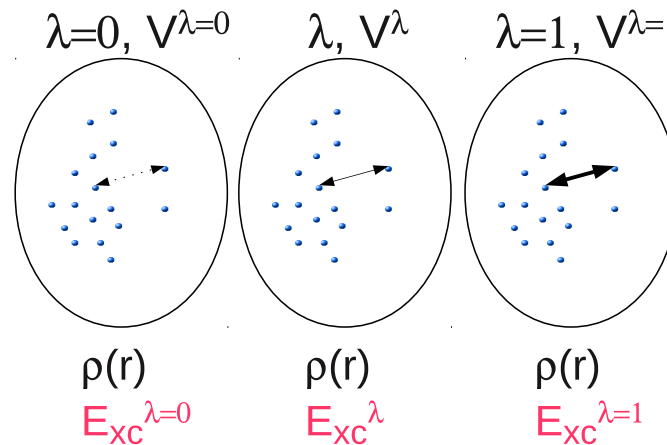
### Jacob's ladder



- DFT heaven
- ...
- ...
- ...
- meta-GGA:  $\dots, \tau(\mathbf{r})$
- GGA:  $\dots, \nabla\rho(\mathbf{r})$
- LSDA:  $\rho(\mathbf{r})$
- Hartree world

”And he dreamed, and behold a ladder set up on the earth, and the top of it reached to heaven...” (Gen 28:12)

# The Hybrid Approximate Functionals



$$E_{xc}^{\lambda} = \int d\mathbf{r}_1 \rho(\mathbf{r}_1) \left[ \int \frac{\rho_{xc}^{\lambda}(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 \right]$$

$$E_{xc} = \int_0^1 \left( \frac{\partial E_{xc}^{\lambda}}{\partial \lambda} \right) d\lambda$$

## The Crudest Hybrid Functional:

$$E_{xc} \approx \frac{1}{2} (E_{xc}^{\lambda=0} + E_{xc}^{\lambda=1})$$

$E_{xc}^{\lambda=0}$  → Exact Hartree-Fock exchange with the Kohn-Sham orbitals

$E_{xc}^{\lambda=1}$  → Exact exchange-correlation functional

## Better Approximate Hybrid Functionals:

$$E_{xc}^{Hybrid} = (1 - a_x)E_x^{DFT} + a_x E_x^{HF} + (1 - a_c)E_c^{DFT} + a_c E_c^{MP2}$$

**Doubly Hybrid Functionals: (final) fifth-rung functionals because they add information about the unoccupied Kohn-Sham orbitals.**



## Doubly hybrid density functional for accurate descriptions of nonbond interactions, thermochemistry, and thermochemical kinetics \*

$$E_{xc}^{R5}[\rho] = E_{xc}^{LDA} + c_2 \Delta E_x^{GGA} + (1 - c_3) \Delta E_c^{GGA} \\ + c_1 (E_x^{HF} - E_x^{LDA}) + c_3 (E_c^{MP2} - E_c^{LDA})$$

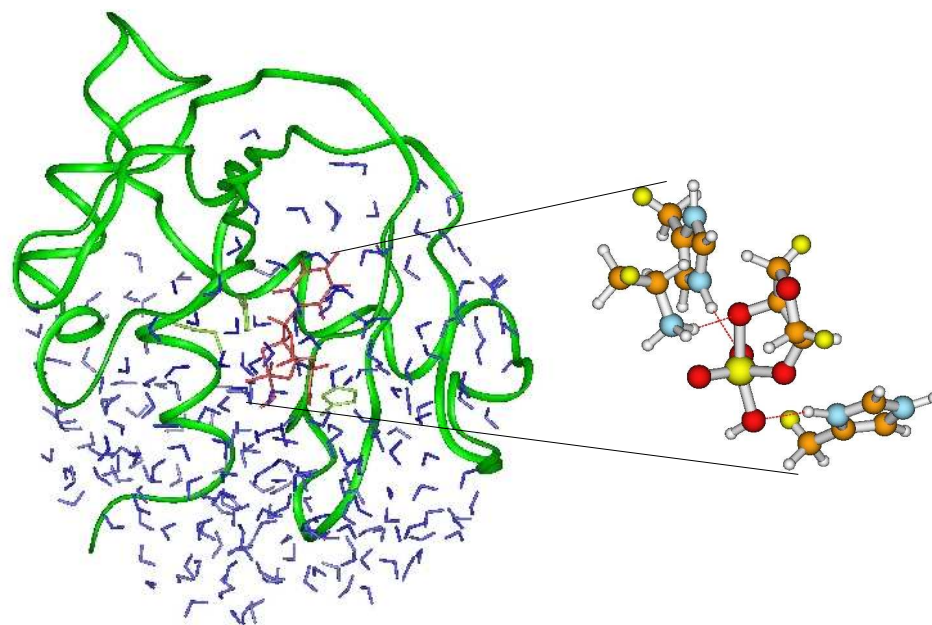
\*Y. Zhanga, X. Xua and W. A. Goddard III; PNAS, **106**, 4963 (2009)

## Computational Performance

Method	VE	SE	DEC	NDEC	CS	size
HF	✓	✓			$K^3-K^4$	50– ~100
DFT/LDA		✓	*		$K^3-K^4$	50– ~500
DFT/GGA		✓	*		$K^3-K^4$	50– ~500
DFT/Hybrid		✓	**		$K^3-K^4$	50– ~500
MP2		✓	*		$K^5$	20–30
MP4		✓	**		$K^7$	10–20
CCSD		✓	**	*	$K^6$	10–30
CCSD(T)		✓	***	*	$K^7$	10–30
CCSDT		✓	***	**	$K^8$	5–15
CIS	✓				$K^4$	50–100
CISD	✓		**		$K^6$	< 10
CISDT	✓		**	*	$K^7$	<10
CISDTQ	✓		***	***	$K^8$	<10
MRCI	✓		***	***	$n \times K^6$	<10
MCSCF	✓	✓	*	***	$n \times K^6$	15–25
full CI	✓	✓	<i>exact</i>	<i>exact</i>	$K!$	< 5

J.M. Mercero, J.M. Matxain, X. Lopez, D.M. York, A. Largo, L. A. Eriksson, J.M. Ugalde; *Int. J. Mas Spectr.* **240**, 37 (2005)

# QM/MM Methods

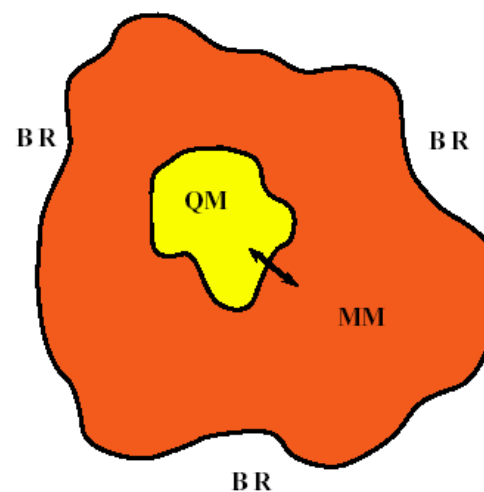


## QM/MM Hamiltonian

For Local Phenomena

$$\hat{H} = \hat{H}_{QM} + \hat{H}_{QM/MM} + \hat{H}_{MM} + \hat{H}_{boundary} + \hat{H}_{restraints}$$

$$\hat{H}_{QM/MM} = \hat{H}_{QM/MM}^{elec} + \hat{H}_{QM/MM}^{vdW} + \hat{H}_{QM/MM}^{bonded}$$



- Warshel, A.; Levitt, M. J. Mol. Biol., **1976**, *103*, 227
- Field, M.J.; Bash, P.A.; Karplus, M. J. Comp. Chem., **1990**, *11*, 700
- Gao, J.; Xio, X. Science **1992**, *258*, 631.
- Tuñón, I.; Martins-Costa, M.T.C.; Milloy, C.; Ruiz-López, M.F.; Rivail, J.-L.; J. Comp. Chem. **1996**, *17*, 19
- Senn, H. M.; Thiel, W. Top. Curr. Chem. **2007**, *268*, 173-290