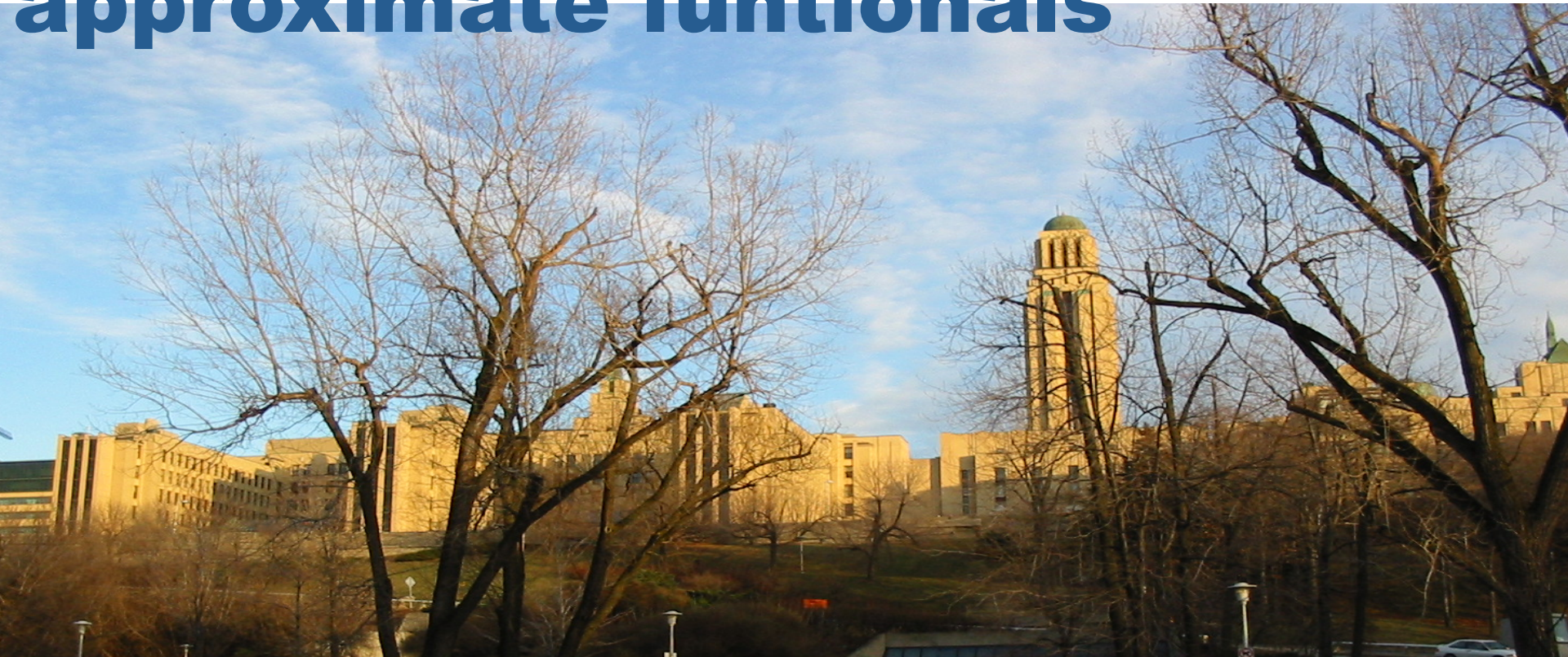


# Introduction to density functional theory and to approximate functionals



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# Introduction

Time-dependant Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \psi = H\psi \quad \langle \psi | \psi \rangle = 1$$

$$H = -\frac{1}{2} \frac{\hbar^2}{m} \sum_{i=1}^N \Delta_i + \sum_{i=1}^N v(\vec{r}_i) + \frac{1}{2} \sum_{i \neq j}^N \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

For molecules, solids, etc.

$$v(\vec{r}) = -\sum_j^n \frac{Z_j e^2}{|\vec{r} - \vec{R}_j|}$$

N=number of electrons  
n=number of nuclei

Density-Functional Theory of Atoms and Molecules, Parr, Yang, Oxford University Press (1989).

Density functional theory, Dreizler, Gross, Springer Verlag, Berlin (1990).

Perdew, Kurth, in Density functionals: Theory and applications, Lecture notes in Physics 500, Springer Verlag, Berlin (1998).

Quantum Theory of the Electron Liquid, Giuliani, Vignale, Cambridge (2005).

We use atomic units

$$e^2 = \hbar = m_e = 1$$

For stationary states

$$\begin{aligned}\Psi &= \Psi(\vec{r}_1 s_1, \vec{r}_2 s_2, \dots, \vec{r}_N s_N, t) \\ &= \Psi(\vec{r}_1 s_1, \dots, \vec{r}_N s_N) e^{-iEt}\end{aligned}$$

$s = \alpha$  or  $\beta$

$$H\Psi = E\Psi$$

# Wave function methods

Variational methods

$$E[\psi] = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}, \quad \delta E[\psi] = 0$$

Perturbation theory

$$\psi = \psi^{(0)} + \psi^{(1)}\lambda + \psi^{(2)}\lambda^{(2)} + \dots$$

Coupled-Cluster theory

$$E = E^{(0)} + E^{(1)}\lambda + E^{(2)}\lambda^{(2)} + \dots$$

Green's function methods

$$G(E) = \frac{1}{H - E + i\eta}$$

Many-body (field theoretical)  
methods

$$W = \ln \text{Tr} \left[ \mathbf{T} e^{-\int_0^\beta d\tau H(\tau)} \right]$$

# Multi-Reference Configuration Interaction Calculations on Cr<sub>2</sub>: Passing the One-Billion Limit in MRCI/MRACPF Calculations

$$\Psi = \sum_i c_i \Phi_i$$

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The chromium dimer, Cr<sub>2</sub>, has been a notoriously difficult molecule to treat computationally and is one example of the difficulties found in providing theoretical treatments for molecules containing first-row transition metal atoms (Salahub 1987). The Cr atom is high spin, d<sup>5</sup>s(7S), and dimerizes to form a low-spin molecule (<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) with the bonding molecular orbitals fully occupied (σ<sub>g</sub><sup>2</sup>, σ<sub>g</sub><sup>2</sup>, π<sub>u</sub><sup>4</sup>, δ<sub>g</sub><sup>4</sup>), which would correspond to a "formal" hextuple bond. The ground state has been established by rotationally resolved measurements of the A←X transition (Efremov et al. 1974; Michalopoulos et al. 1982; Riley et al. 1983). The vibrational frequency is relatively high at 452 cm<sup>-1</sup> consistent with the formal high-bond order, as is the quite short bond length of 1.679 Å (Bondybey and English 1983). A modified RKR (Rydberg-Klein-Rees) potential energy curve for Cr<sub>2</sub> has been developed based on negative-ion photoelectron spectroscopy of Cr<sub>2</sub><sup>-</sup> and shows interesting structural features, notably a "shelf" region at higher vibrational energy levels (Casey and Leopold 1993). However, the binding energy is not all that high for such a hextuple bond with the best experimental value giving 1.44 ± 0.05 eV (Hilpert and Ruthardt 1987). The region around the minimum of the potential energy curve of Cr<sub>2</sub> has been calculated at the multireference configuration interaction (CI) level, including almost 1.3 billion configurations in the CI calculation. Novel computational techniques were implemented on massively parallel computers to enable this calculation. The calculated results are R<sub>e</sub> = 1.72 Å, D<sub>e</sub> = 1.09 eV, and ω<sub>e</sub> = 338.7 cm<sup>-1</sup> compared with experimental values of R<sub>e</sub> = 1.679 Å, D<sub>e</sub> = 1.50 ± 0.05 eV, and ω<sub>e</sub> = 452.34(ΔG<sub>1,2</sub>) cm<sup>-1</sup>. The error of 0.4 eV in the dissociation energy can be attributed to relativistic effects following other authors (0.2 eV) and the need for higher angular momentum basis functions in the 1-particle set (0.2 eV).

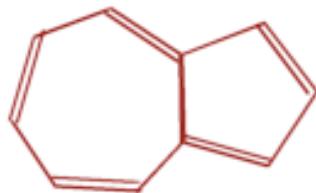
# Electron density

$$\rho(\vec{r}_1) = N \int d^3 r_2 \dots d^3 r_N d\sigma_1 \dots d\sigma_N$$

$$\times \psi^*(\vec{r}_1, \sigma_1, \dots, \vec{r}_N, \sigma_N) \psi(\vec{r}_1, \sigma_1, \dots, \vec{r}_N, \sigma_N)$$

$$\rho(\vec{r}_1, \sigma_1) = N \int d^3 r_2 \dots d^3 r_N d\sigma_2 \dots d\sigma_N$$

$$\times \psi^*(\vec{r}_1, \sigma_1, \dots, \vec{r}_N, \sigma_N) \psi(\vec{r}_1, \sigma_1, \dots, \vec{r}_N, \sigma_N)$$



Azulene

$$\langle \psi | \sum_{i=1}^N v(\vec{r}_i) | \psi \rangle = \int d^3 r \rho(\vec{r}) v(\vec{r})$$

# The ground-state variational method in

$$E[\psi] = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

$$E = \min_{\psi} \langle \psi | T + v + V_{ee} | \psi \rangle$$

$$= \min_{\psi} \left\{ \overbrace{\int d^3r \rho(\vec{r})v(\vec{r})}^{\nearrow} + \langle \psi | T + V_{ee} | \psi \rangle \right\}$$

$$E = \min_{\rho} \min_{\psi \rightarrow \rho} \left\{ \int d^3r \rho(\vec{r})v(\vec{r}) + \langle \psi | T + V_{ee} | \psi \rangle \right\}$$

$$= \min_{\rho} \left\{ \int d^3r \rho(\vec{r})v(\vec{r}) + \min_{\psi \rightarrow \rho} \langle \psi | T + V_{ee} | \psi \rangle \right\}$$

$$F[\rho] = \min_{\psi \rightarrow \rho} \langle \psi | T + V_{ee} | \psi \rangle$$

$$E = \min_{\rho} \left\{ \int d^3r \rho(\vec{r})v(\vec{r}) + F[\rho] \right\}$$

Hohenberg, Kohn, PR 136B, 864 (1964)

M. Levy, Proc. Natl. Acad. Sci, USA 79, 6062 (1979)

M. Levy, PRA 26, 1200 (1982)

$$F[\rho] = E - \underbrace{\int d^3r \frac{\delta E}{\delta v(\vec{r})}}_{\rho(\vec{r})} v(\vec{r})$$

$$T = C_F \int d^3r \rho^{5/3}(\vec{r})$$

Thomas&Fermi (1927)

# Slater determinant

$$\phi(1,2,\dots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) & \varphi_1(2) & \cdots & \varphi_1(N) \\ \varphi_2(1) & \varphi_2(2) & & \\ \vdots & & \ddots & \vdots \\ \varphi_N(1) & & \cdots & \varphi_N(N) \end{vmatrix}$$

$$\phi(1,2,\dots,N) = \frac{1}{\sqrt{N!}} \det \{ \varphi_1(1) \times \varphi_2(2) \dots \varphi_N(N) \}$$

$$\frac{1}{\sqrt{N!}} \det \{ \varphi_1(1) \dots \varphi_N(N) \} = \frac{1}{\sqrt{N!}} \sum_P \text{Sign}(P) P \{ \varphi_1(1) \dots \varphi_N(N) \}$$



# Hartree-Fock energy

$$E^{HF} = \langle \phi^{HF} | T | \phi^{HF} \rangle + \int d^3 r \rho^{HF}(\vec{r}) v(\vec{r}) + \frac{1}{2} \int d^3 r d^3 r' \frac{\rho^{HF}(\vec{r}) \rho^{HF}(\vec{r}')}{|\vec{r} - \vec{r}'|} \\ - \sum_{\sigma} \sum_{ij} \frac{1}{2} \int d^3 r d^3 r' \frac{\varphi_{i,\sigma}^{HF*}(\vec{r}) \varphi_{j,\sigma}^{HF}(\vec{r}) \varphi_{i,\sigma}^{HF}(\vec{r}') \varphi_{j,\sigma}^{HF*}(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

Kohn-Sham expression for the ground-state energy

$$E = \langle \psi | T + v + V_{ee} | \psi \rangle = \int d^3 r \rho(\vec{r}) v(\vec{r}) + T + V_{ee}$$

$$E = \int d^3 r \rho(\vec{r}) v(\vec{r}) + \underbrace{\langle \phi^{KS} | T | \phi^{KS} \rangle + \frac{1}{2} \int d^3 r d^3 r' \frac{\rho(\vec{r}') \rho(\vec{r})}{|\vec{r} - \vec{r}'|}}_{F[\rho]} + E_{xc}[\rho]$$

$$E = \int d^3r \rho(\vec{r}) v(\vec{r}) + T_s[\rho] + U[\rho] + E_{xc}[\rho]$$

$$T_s[\rho] = \sum_i^N \int d^3r \varphi_i^{KS}(\vec{r}) \left( -\frac{1}{2} \Delta_{\vec{r}} \right) \varphi_i^{KS}(\vec{r})$$

$$= \min_{\phi^{KS} \rightarrow \rho} \langle \phi^{KS} | T | \phi^{KS} \rangle$$

Single-particle kinetic energy

$$U[\rho] = \frac{1}{2} \int d^3r d^3r' \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

Interaction of the electron density with itself

$$E_{xc}[\rho] = T - T_s + V_{ee} - U$$

$$= F - T_s - U$$

Exchange-correlation energy

# Kohn-Sham equations

$$E = \int d^3 r \rho(\vec{r}) v(\vec{r}) + T_S[\rho] + U[\rho] + E_{XC}[\rho]$$

$$\frac{\delta E}{\delta \rho} = 0 \Leftrightarrow \frac{\delta E}{\delta \varphi_i^{KS}} = 0$$

$$\left( -\frac{1}{2} \Delta + v_s(\vec{r}) \right) \varphi_i^{KS}(\vec{r}) = \varepsilon_i \varphi_i^{KS}(\vec{r})$$

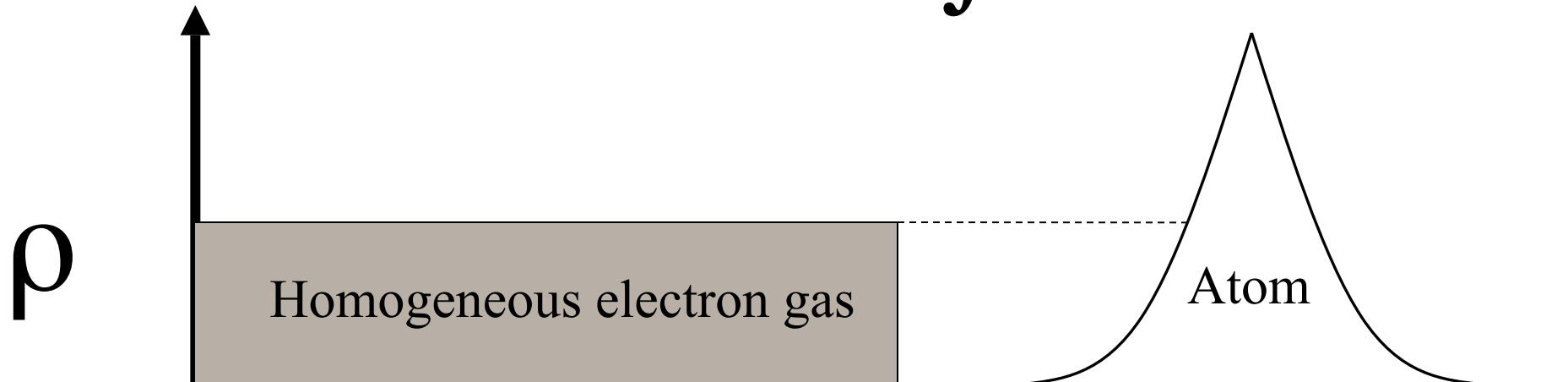
$$v_S(\vec{r}) = v(\vec{r}) + \int d^3 r' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + v_{XC}(\vec{r})$$

$$v_{XC}(\vec{r}) = \frac{\delta E_{XC}}{\delta \rho(\vec{r})}$$

# Local density approximation to the exchange-correlation energy

$$e_{XC}^{LDA}(\rho) = E_{XC}^{\text{hom}}(\rho) / V$$

$$E_{XC}^{LDA} = \int d^3 r e_{XC}^{LDA}(\rho(\vec{r}))$$



# Local density approximation to the exchange energy

$$E_{XC} = E_X + E_C$$

$$E_x = -\frac{1}{2} \sum_{\sigma} \sum_{i,j}^{occ} \int d^3r d^3r' \frac{\varphi_i^{\sigma}(\vec{r}) \varphi_j^{\sigma}(\vec{r}) \varphi_i^{\sigma}(\vec{r}') \varphi_j^{\sigma}(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

$$e_X^{LDA}(\vec{r}) = C^{(X)} \rho^{4/3}(\vec{r})$$

$$E_X^{LDA} = \int d^3r e_X^{LDA}(\vec{r})$$

# Gradient expansion approximation (GEA)

$$G[\rho] = \int d^3 r g(\vec{r}, [\rho])$$

$$\begin{aligned} g([\rho]) &= g_{00}(\rho(\vec{r})) + g_{22}(\rho(\vec{r}))(\nabla\rho(\vec{r}))^2 \\ &+ g_{42}(\rho(\vec{r}))(\Delta\rho(\vec{r}))^2 + g_{42}(\rho(\vec{r}))(\Delta\rho(\vec{r}))(\nabla\rho(\vec{r}))^2 \\ &+ g_{44}(\rho(\vec{r}))(\nabla\rho(\vec{r}))^2(\nabla\rho(\vec{r}))^2 + \dots \end{aligned}$$

$$E_X^{GEA} = C^{(X)} \int d^3 r \rho^{4/3} + C_{21}^{(X)} \int d^3 r \frac{|\nabla\rho|^2}{\rho^{4/3}} + \dots$$

# Generalized gradient approximation (GGA)

$$\begin{aligned} E_X^{GGA} &= C^{(X)} \int d^3 r \rho^{4/3} + C_{21}^{(X)} \int d^3 r \frac{|\nabla \rho|^2}{\rho^{4/3}} + \dots \\ &= C^{(X)} \int d^3 r \rho^{4/3} F_X^{GGA}(x) \end{aligned}$$

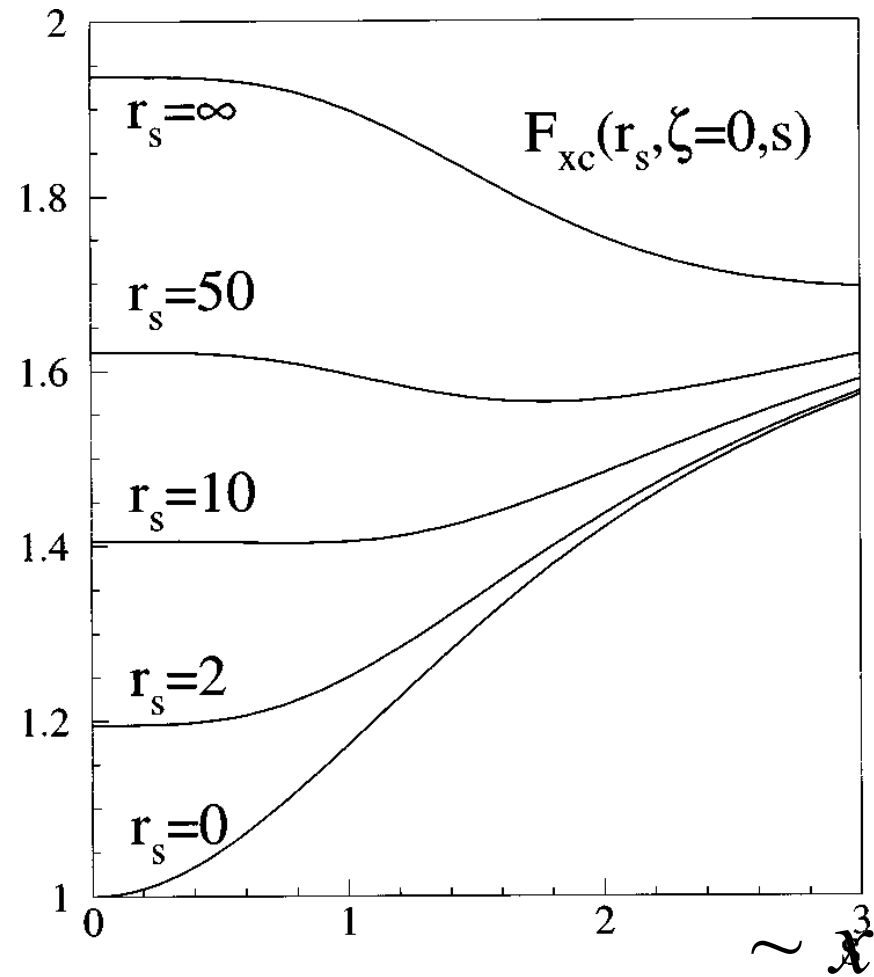
with

$$F_X^{GGA}(x) = 1 + \frac{C_{21}^{(X)}}{C^{(X)}} x^2, \quad x = \frac{|\nabla \rho|}{\rho^{4/3}}$$

$$F_X^{GGA} \text{ (R) } F_X^{GGA} = 1 + c_1 x^2 + c_2 x^4 + \dots$$

$$E_X^{exact} \geq -1.679 \int d^3r \rho^{4/3}(\vec{r})$$

$$F_X^{GGA}(x) \text{ \textcircled{R} } F_X^{GGA}(x)$$





# Perdew-Burke-Ernzerhof (PBE)

PBE generalized gradient approximation:

$$E_{XC}^{PBE}[\rho] = \int d^3r f(\rho(\vec{r}), \nabla\rho(\vec{r}))$$

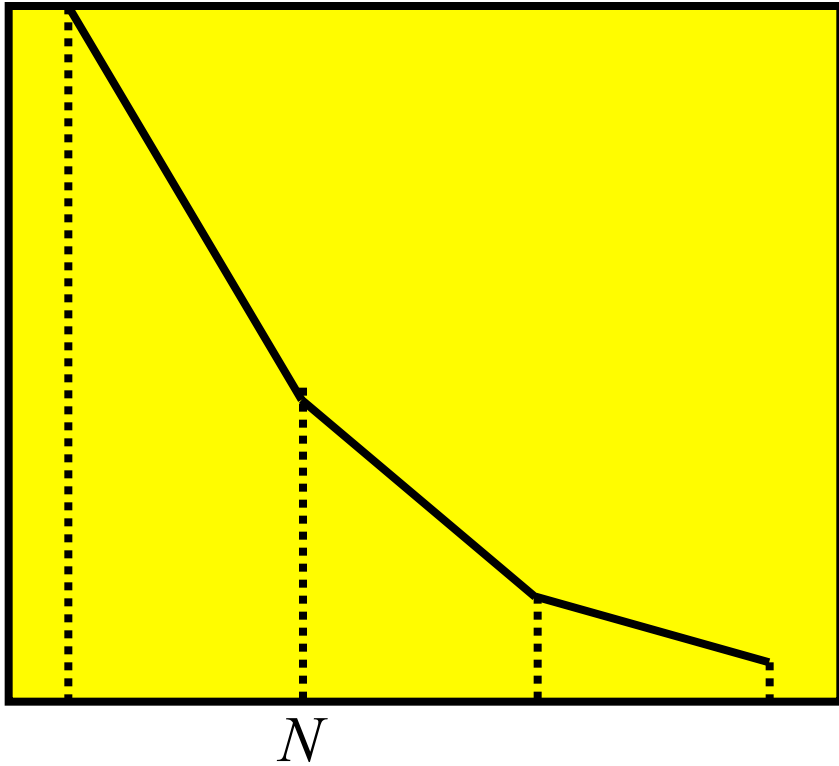
Perdew, Burke, Ernzerhof,  
Phys. Rev. Lett. 77, 3865 (1996)

# Results

System	$\Delta E^{\text{UHF}}$	$\Delta E^{\text{LSD}}$	$\Delta E^{\text{PW91}}$	$\Delta E^{\text{PBE}}$	$\Delta E^{\text{expt}}$
H <sub>2</sub>	84	113	105	105	109
LiH	33	60	53	52	58
CH <sub>4</sub>	328	462	421	420	419
NH <sub>3</sub>	201	337	303	302	297
OH	68	124	110	110	107
H <sub>2</sub> O	155	267	235	234	232
HF	97	162	143	142	141
Li <sub>2</sub>	3	23	20	19	24
LiF	89	153	137	136	139
Be <sub>2</sub>	-7	13	10	10	3
C <sub>2</sub> H <sub>2</sub>	294	460	415	415	405
C <sub>2</sub> H <sub>4</sub>	428	633	573	571	563
HCN	199	361	326	326	312
CO	174	299	269	269	259
N <sub>2</sub>	115	267	242	243	229
NO	53	199	171	172	153
O <sub>2</sub>	33	175	143	144	121
F <sub>2</sub>	-37	78	54	53	39
P <sub>2</sub>	36	142	120	120	117
Cl <sub>2</sub>	17	81	64	63	58
Mean abs. error	71.2	31.4	8.0	7.9	...

# Dependence of the energy on N

$E(N)$



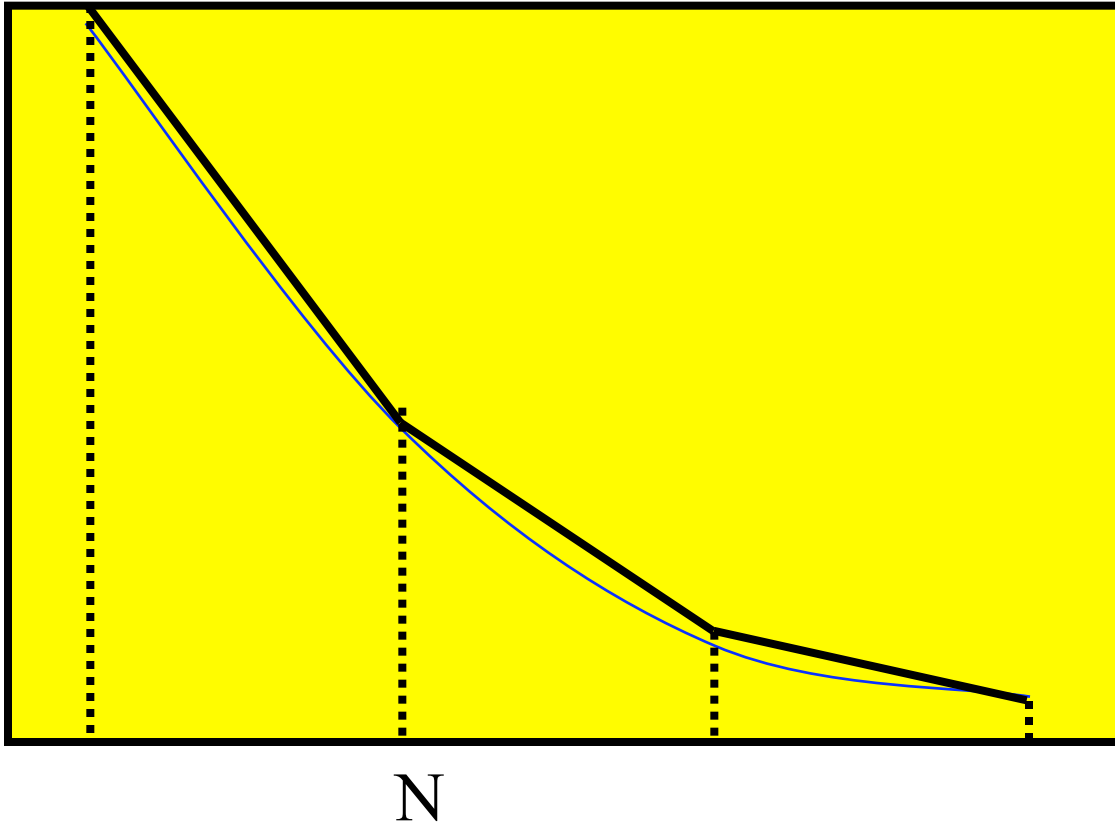
$$E = T_s[\rho] + \int d^3r \rho(\vec{r}) v(\vec{r}) + \frac{1}{2} \int d^3r d^3r' \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + E_{xc}[\rho]$$

Perdew, Parr, Levy, Balduz, PRL 49, 1691 (1982)

$$\underbrace{\frac{\partial E(N)}{\partial N} \Big|_{N+\delta}}_{=-EA} - \underbrace{\frac{\partial E(N)}{\partial N} \Big|_{N-\delta}}_{=-IP} = \frac{\partial T_s(N)}{\partial N} \Big|_{N+\delta} - \frac{\partial T_s(N)}{\partial N} \Big|_{N-\delta} + \frac{\partial E_{xc}(N)}{\partial N} \Big|_{N+\delta} - \frac{\partial E_{xc}(N)}{\partial N} \Big|_{N-\delta}$$

# Dependence of the energy on N

$E(N)$

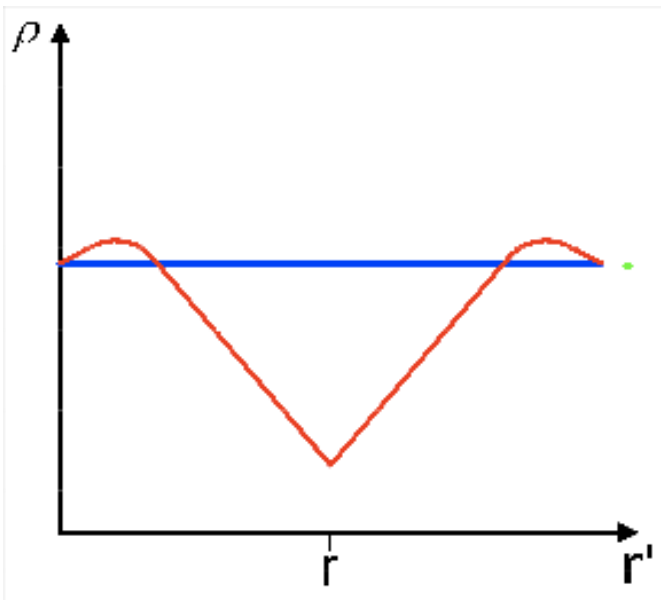


$$\frac{\partial E(N)}{\partial N} \Big|_{N-\delta} = -IP$$
$$= \epsilon_{\max}$$

Janak, PRB 18, 7165 (1978)

# Exchange-correlation hole surrounding an electron

$$V_{ee} + T_C = \frac{1}{2} \int d^3r d^3r' \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + E_{xc}[\rho]$$



$$V_{ee} + T_C = \frac{1}{2} \int d^3r d^3r' \frac{\rho(\vec{r}) \left( \rho(\vec{r}') + \rho_{xc}(\vec{r}, \vec{r}') \right)}{|\vec{r} - \vec{r}'|}$$

$$E_{xc}[\rho] = \frac{1}{2} \int d^3r d^3r' \frac{\rho(\vec{r}) \rho_{xc}(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|}$$

Ernzerhof, Perdew, Burke, Topics in Current Chemistry Vol. 180, Springer (1996)  
 Burke, Perdew, Ernzerhof, J. Chem. Phys. 109, 3760 (1998)

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