Generalized Gradient Approximation Made Simple: The PBE Density Functional

Rick Muller
Quantum Chemistry Group
Materials and Process Simulation Center
May 2000

Density Functional Theory

- $H = T + V_N + V_J + V_X + V_C$
  - T, V_N, V_J are identical to their HF counterparts
  - V_X is the Exchange Functional
  - V_C is the Correlation Functional
- Local Density Approximation
  - Simplest Approximation
  - Consider only the density at any point in space
- Generalized Gradient Approximation
  - More Accurate Approximation
  - Consider both the density and the gradient of the density

Terms in Density Functionals

ρ	Local density
r_s	Seitz radius = $(3/4\pi\rho)^{1/3}$
k_F	Fermi wave number = $(3\pi^2\rho)^{1/3}$
t	Density gradient = $\lvert\text{grad } \rho\rvert/2\phi k_s\rho$
ζ	Spin polarization = $(\rho_{up} - \rho_{down})/\rho$
ϕ	Spin scaling factor = $[(1+\zeta)^{2/3} + (1-\zeta)^{2/3}]/2$
k_s	Thomas-Fermi screening wave number = $(4k_F/\pi a_0)^{1/2}$
s	Another density gradient = $\lvert\text{grad } \rho\rvert/2k_F\rho$

Local Density Approximation

$$E_X^{LDA} = \int \rho(r)\varepsilon_X^{LDA}(r)d^3r$$

$$E_C^{LDA} = \int \rho(r)\varepsilon_C^{LDA}(r)d^3r$$

$$\varepsilon_X^{LDA}(r) = \frac{-3e^2k_F}{4\pi}$$

$$\varepsilon_C^{LDA} = F[r_s]$$

Local Spin Density Approximation

$$\varepsilon_X^{LSD}[\rho_\uparrow + \rho_\downarrow] = \frac{\rho_\uparrow \varepsilon_X^{LSD}[2\rho_\uparrow] + \rho_\downarrow \varepsilon_X^{LSD}[2\rho_\downarrow]}{\rho_\uparrow + \rho_\downarrow}$$

$$\varepsilon_C^{LSD} = F[r_s, \zeta]$$

Local Spin Density Correlation Functional

- Not for the faint of heart:

$$\varepsilon_C^{LSD}[r_s,\zeta] = e_u(1-\phi'\zeta^4) + e_p(1-\phi'\zeta^4) - \frac{\alpha_m \phi'(1-\zeta^4)}{f_{zz}}$$

$$e_u = G_{corr}(0.0310907, 0.21370, 7.5957, 3.5876, 1.6382, 0.4294, r_s^{1/2})$$

$$e_p = G_{corr}(0.01554535, 0.20548, 14.1189, 6.1977, 3.3662, 0.62517, r_s^{1/2})$$

$$\alpha_m = G_{corr}(0.0168869, 0.11125, 10.357, 3.6231, 0.88026, 0.49671, r_s^{1/2})$$

$$\phi' = \left[(1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2\right]/\gamma$$

$$\gamma = 0.5198421$$

$$f_{zz} = 1.709921$$

$$G_{corr}(a, a_1, b_1, b_2, b_3, b_4, r) = -2a(1+a_1 r^2)\log\left[1 + \frac{1}{2ar(b_1 + r(b_2 + r(b_3 + b_4 r)))}\right]$$

Generalized Gradient Approximation Functionals

- The GGA Correlation functional has the form

$$E_C^{GGA}[\rho_\uparrow, \rho_\downarrow] = \int \rho(r)\{\varepsilon_C^{LDA}(r_s, \zeta) + H(r_s, \zeta, t)\}d^3r$$

- The GGA Exchange functional has the form

$$E_X^{GGA} = \int \rho(r)\varepsilon_X^{LDA}(\rho)F_X(s)d^3r$$

Limits the Correlation Functional Must Obey

- Slowly Varying Limit

$$\lim_{t\to 0} H = \frac{e^2}{a_0}\beta\phi^3 t^2$$

- Rapidly Varying Limit

$$\lim_{t\to \infty} H = -\varepsilon_C^{unif}$$

- Uniform Scaling to High Density Limit

$$\lim_{t\to \infty} H = -\varepsilon_C^{unif}$$

Correlation: Slowly Varying Limit

Correlation: Rapidly Varying Limit

Correlation: Uniform Scaling to High Density Limit

PBE Correlation Correction Form

Limits the Exchange Functional Must Obey

- Uniform Scaling to High Density Limit
- Spin Scaling Relationship
- Lieb-Oxford Bound

Exchange: Uniform Scaling to High Density Limit

Exchange: Spin Scaling Relationship

Exchange: Small Density Variations Must Reproduce Uniform Density Limit

Lieb-Oxford Bound

PBE Exchange Correction Form

Comparison of Density Functionals

References

J. P. Perdew, K. Burke, M. Enzerhof. "Generalized Gradient Approximation Made Simple." PRL **77**, 3865 (1996)

J. P. Perdew, in "Electronic Structure of Solids '91." P. Ziesche, H. Eschrig eds. (Akademie Verlag, Berlin, 1991), p. 11.

B. G. Johnson, P. M. W. Gill, J. A. Pople. "The Performance of a Family of Density Functionals." JCP **98**, 5612 (1993).

T. Ziegler. "Approximate Density Functional Theory as a Practical Tool in Molecular Energetics and Dynamics." Chem. Rev. **91**, 651 (1991).

T. V. Russo, R. L. Martin, P. J. Hay. "Density Functional Calculations on First-Row Transition Metals." JCP **101**, 7729 (1994).