

Quaccs 2016: Density-functional theory for molecules

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This workshop aims at illustrating how to compute exchange-correlation energies within density-functional theory. Part of this document has been generously provided by Peter Gill, and was part of his workshop at the previous Quaccs conference in 2014.

I. EXCHANGE-CORRELATION ENERGY

According to density-functional theory (DFT) [1], the exchange (x) and correlation (c) energies can be written as functionals of the electron density $\rho(\mathbf{r})$ of a system. In most approximate functionals, these energies are written as integrals of functions of the density, for example

$$E_x = \int e_x[\rho(\mathbf{r})] d\mathbf{r} \quad (1)$$

and this allows the exchange (or correlation) energy to be computed much more quickly than by other methods (e.g. Hartree-Fock theory, perturbation theory, coupled cluster theory, etc.) The not-so-good news is that the DFT estimates are approximate and, sometimes, they can be far from the true values.

A. Radial Quadrature

There are many possible ways to estimate a general radial integral from 0 to ∞ . One of these is the Euler-Maclaurin quadrature developed by Boys and Handy and given by

$$\int_0^\infty r^2 f(r) dr \approx \sum_{i=1}^m w_i f(r_i) \quad (2)$$

where the roots and weights are

$$r_i = Ri^2(m+1-i)^{-2} \quad (3)$$

$$w_i = 2R^3(m+1)i^5(m+1-i)^{-7} \quad (4)$$

The parameter R is a scaling variable that allows the quadrature to be tailored to a particular integral. If it is well chosen, it can lead to more accurate results with few quadrature points. We will assume (at least initially) that $R = 1$.

Of course, the accuracy of these approximations depends on the number m of points and the function $f(r)$. However, it has been found to be reasonably effective for many of the radial integrals that arise in DFT calculations.

You have been given a FORTRAN subroutine called EULMAC which computes these roots and weights for any desired values of m and R .

B. Angular Quadrature

There are many possible ways to estimate a general angular integral over the surface of a unit sphere S . One of these is the quadrature developed by Lebedev, which extends the familiar octahedral 6-point rule. It is given by

$$\int_S g(x, y, z) d\Omega \approx \sum_{j=1}^M W_j g(x_j, y_j, z_j) \quad (5)$$

where the roots (x_j, y_j, z_j) and weights W_j are chosen so that the quadrature is exact for as many low-degree spherical harmonics as possible.

Of course, the accuracy of these approximations depends on the number M of points and the function $g(x, y, z)$. However, it has been found to be reasonably effective for many of the radial integrals that arise in DFT calculations.

You have been given a FORTRAN subroutine called LEBDEV which computes these roots and weights for any desired value of M .

C. Quadrature in 3D

In typical DFT calculations, we are faced with integrals over all space

$$I = \int F(\mathbf{r}) d\mathbf{r} \quad (6)$$

If an atomic nucleus forms a natural origin, we can express this integral in terms of spherical polar coordinates and then estimate the radial and angular integrals using the quadratures described above, *i.e.*

$$I = \int_0^\infty \int_0^\pi \int_0^{2\pi} F(r, \theta, \phi) r^2 \sin \theta d\phi d\theta dr \quad (7)$$

$$\approx \sum_{i=1}^m \sum_{j=1}^M w_i W_j F(r_i, \theta_j, \phi_j) \quad (8)$$

You have been given a FORTRAN program that uses this approximation to estimate the number of electrons in the ground-state hydrogen atom by integrating its elec-

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tron density $\rho(r) = \psi_{\text{H}}(r)^2$ over all space, *i.e.*

$$n = \int \rho(\mathbf{r}) d\mathbf{r} \quad (9)$$

$$= \int_0^\infty \int_0^\pi \int_0^{2\pi} \frac{\exp(-2r)}{\pi} r^2 \sin\theta d\phi d\theta dr \quad (10)$$

where

$$\psi_{\text{H}}(r) = \frac{1}{\sqrt{\pi}} \exp(-r) \quad (11)$$

Exercise 1: Explore the effects of using various numbers of radial and angular points. How many points are required to estimate the number of electrons correctly to within 10^{-3} ? How many are required to obtain 10^{-6} accuracy?

Exercise 2: Perform a similar study on the helium atom with density

$$\rho_{\text{He}}(r) = \frac{19683}{2048\pi} \exp\left(-\frac{27}{8}r\right) \quad (12)$$

II. EXCHANGE FUNCTIONALS

A. Dirac–Slater exchange functional

The famous Dirac–Slater exchange functional (which is the exchange part of the LDA) is [1]

$$E_x^{\text{LDA}}[\rho_\alpha(\mathbf{r})] = -\frac{3}{2} \left(\frac{3}{4\pi}\right)^{1/3} \int \rho_\alpha(\mathbf{r})^{4/3} d\mathbf{r} \quad (13)$$

where $\rho_\alpha(\mathbf{r})$ is the density of the α (or spin-up) electrons.

Exercise 3: Modify the FORTRAN program to compute the LDA exchange energy of the hydrogen and helium atoms. The true (Fock) exchange energies can be found in Ref. [2]. How well does the LDA functional perform using a large grid?

B. Becke 88 exchange functional

The famous 1988 Becke exchange functional (which is the exchange part of BLYP) is [3]

$$E_x^{\text{B88}}[\rho_\alpha(\mathbf{r}), x_\alpha(\mathbf{r})] = E_x^{\text{LDA}}[\rho_\alpha(\mathbf{r})] - \beta \int \frac{\rho_\alpha(\mathbf{r})^{4/3} x_\alpha(\mathbf{r})^2}{1 + 6\beta x_\alpha(\mathbf{r}) \sinh^{-1} x_\alpha(\mathbf{r})} d\mathbf{r} \quad (14)$$

where $\beta = 0.0042$ and the reduced density gradient is defined by

$$x_\alpha(\mathbf{r}) = \frac{|\nabla\rho_\alpha(\mathbf{r})|}{\rho_\alpha(\mathbf{r})^{4/3}} \quad (15)$$

Exercise 4: Derive an expression for the reduced density gradient of the hydrogen and helium atoms and use this to compute its B88 exchange energy. How much more accurate is it than the LDA estimate above?

III. CORRELATION FUNCTIONALS

A. LDA correlation functional

The 1980 WVN correlation functional (which is the correlation part of the LDA) is defined in Ref. [4]. Because it is a very messy functional, I am going to provide the fortran code to calculate the LDA correlation energy for the hydrogen and helium atom.

Exercise 5: Using the hydrogen and helium atoms again, compute the LDA correlation energies. How does it compare with the exact values given in Ref. [5]?

B. LYP correlation functional

For a closed-shell system like the helium atom, the very famous LYP correlation functional is defined as [5]:

$$e_c^{\text{LYP}}(\rho) = -a \frac{\rho^{-1}}{1 + d\rho^{-1/3}} \left\{ \rho + b\rho^{-2/3} \left[C_F \rho^{5/3} - 2t_W + \left(\frac{t_W}{9} + \frac{\nabla^2 \rho}{18} \right) \right] e^{-c\rho^{-1/3}} \right\} \quad (16)$$

where

$$t_W = \frac{|\nabla\rho|^2}{8\rho} - \frac{\nabla^2\rho}{8} \quad (17)$$

$$C_F = \frac{3}{10} (3\pi^2)^{2/3} = 2.871234 \quad (18)$$

and $a = 0.04918$, $b = 0.132$, $c = 0.2533$ and $d = 0.349$ are fitting parameters.

Exercise 6: Compute the LYP correlation energies for the helium atom. How does it compare with the LDA value and exact value given in Ref. [5]?

IV. EXCHANGE-CORRELATION FUNCTIONALS

A. BLYP exchange-correlation functional

The BLYP correlation functional combines the B88 exchange functional and the LYP correlation functional [6].

Exercise 7: Combining the previous results, compute the BLYP exchange-correlation energy of the helium

atom.

B. B3LYP exchange-correlation hybrid functional

The extremely famous B3LYP exchange-correlation functional combines the B88 and LDA exchange functionals with the LDA and LYP correlation functionals, adding on top of this some (exact) Fock exchange [7]. Its usual definition is

$$E_{xc}^{\text{B3LYP}} = E_{xc}^{\text{LDA}} + a_0 \Delta E_x^{\text{exact}} + a_x \Delta E_x^{\text{B88}} + a_c \Delta E_c^{\text{LYP}} \quad (19)$$

where

$$\Delta E_x^{\text{exact}} = E_x^{\text{exact}} - E_x^{\text{LDA}} \quad (20)$$

$$\Delta E_x^{\text{B88}} = E_x^{\text{B88}} - E_x^{\text{LDA}} \quad (21)$$

$$\Delta E_c^{\text{LYP}} = E_c^{\text{LYP}} - E_c^{\text{LDA}} \quad (22)$$

and

$$a_0 = 0.20 \quad a_x = 0.72 \quad a_c = 0.81 \quad (23)$$

Exercise 8: Combining the previous results, compute the B3LYP exchange and correlation energies of the helium atom.

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