Exact exchange functional for the hydrogen atom

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We have constructed a gradient-corrected exchange functional which, when used in a self-consistent Kohn-Sham procedure, gives the exact Schrödinger energy and density for the hydrogen atom. The functional bears very little resemblance to any of the commonly used exchange functionals, even in its asymptotic behavior.

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Both density-functional theory [1] (DFT) and traditional ab initio theory [2] can be used to determine approximate wave functions and total energies for inhomogeneous many-electron systems. The most significant difference between their approaches is that in DFT, the exchange and correlation energies are computed as functionals of the electron density. This strategy reduces the computational cost of the calculations very significantly but, of course, the accuracy of the total energies obtained is critically dependent on the quality of the functionals employed. Recent years, however, have witnessed the advent of some remarkably competent exchange [3] and correlation [4–6] functionals which have sparked great interest in DFT as a tool for computational chemistry.

Because the exchange interaction involves only same-spin electrons, the DFT exchange energy is commonly expressed as a sum

$$E_X = \int E(\rho_{\alpha}, |\nabla \rho_{\alpha}|) dV + \int E(\rho_{\beta}, |\nabla \rho_{\beta}|) dV$$

(1)

of integrals of functions of the electronic densities $\rho_{\alpha}$ and $\rho_{\beta}$ and their gradients. While the function $E$, which is exact for the uniform electron gas

$$E^{\text{Dirac}}(\rho) = -\frac{3}{2} \left( \frac{3}{4\pi} \right)^{1/3} \rho^{4/3}$$

(2)

has been known for many years [7], its deficiencies when applied to inhomogeneous systems such as molecules are also well known. Modifications of (2), which perform better in such systems and which usually include gradient corrections, have therefore been vigorously pursued.

Although the best way in which to include the gradient remains an open question, a particularly fruitful suggestion was made by Becke [3]. His approach, which has been widely embraced, was to require that the function $E$ be exact not only for the uniform electron gas but also for the exchange energy density at points asymptotically distant from the system. In Becke's model, this leaves one free parameter (dictating how quickly the asymptotic behavior is approached), which he chose to fit the known exchange energies of the inert gases.

Many exchange functionals can be written as

$$\int E(\rho, |\nabla \rho|) dV = \int \rho^{4/3} g(x) dV$$

(3)

where

$$x = |\nabla \rho|/\rho^{4/3}$$

(4)

and, henceforth, we will confine our attention to this class of functionals. For example, the uniform gas functional is obtained from

$$g^{\text{Dirac}}(x) = -\frac{3}{2} \left( \frac{3}{4\pi} \right)^{1/3}$$

(5)

the “almost uniform” gas [8] functional is obtained from

$$g^{\text{Sham}}(x) = g^{\text{Dirac}}(x) - \frac{7}{16}(81\pi^3)^{-1/3}x^2$$

(6)

and Becke’s 1988 functional (wide infra) is obtained from

$$g^{\text{Becke}}(x) = g^{\text{Dirac}}(x) - \frac{b x^2}{1 + 6 b x \sinh^{-1} x}$$

(7)

using $b = 0.0042$. Using the calculus of variations, it is straightforward to show that the exchange potential that results from (3) is given by

$$V_X = \frac{3}{2} \rho^{1/3} \left[ g - \frac{d}{dx} \frac{d^2 g}{dx^2} \right] - \frac{\nabla^2 \rho}{|\nabla \rho|} \frac{d g}{dx}$$

$$+ \frac{(\nabla \rho)^T H_{\rho}(\nabla \rho)}{|\nabla \rho|^{3/2}} \frac{d g}{dx} - x \frac{d^2 g}{dx^2}$$

(8)

where $H_{\rho}$ is the second-derivative matrix (Hessian) of the density. (We note that an equivalent expression has previously been derived by Perdew and Wang [9].) We will use (8) to find an exact [10] exchange functional for the hydrogen atom.

The exact ground-state density of the hydrogen atom is known to be

$$\rho = \pi^{-1} e^{-x}$$

(9)

where $x = 2r$, from which expressions for $|\nabla \rho|$, etc., for example,

$$x = (2\pi^{1/3}) e^{x/3}$$

(10)

are easily derived. Substituting such expressions into (8) yields

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\[ V_x^H = \frac{2x}{3} \frac{d^2 g}{dx^2} + \left[ \frac{4}{3} - \frac{8}{3} \right] \frac{dg}{dx} + \frac{8}{3x} g , \]  
(11)

which is the hydrogen atom exchange potential implied by any \( g(x) \). But, in an exact DFT treatment, this should precisely cancel the DFT Coulomb potential

\[ V_J^H = \int \frac{\rho(a)}{|r-a|} da = \frac{2}{z} \ln \left( 1 + \frac{2}{z} \right) \]  
(12)

of the spurious electronic self-interaction. Therefore a necessary condition for a function \( g(x) \) to give, through (3), an exact exchange functional for the hydrogen atom is that it make (11) and (12) equal and opposite, i.e.,

\[ \frac{d^2 g}{dz^2} + \left[ \frac{2}{z} - \frac{5}{3} \right] \frac{dg}{dz} = 4g - 4 \pi \right]^{1/3} e^{z^{1/3}} \]  
(13)

Introducing a new dependent variable \( w \) defined by

\[ g(x) = -xw(z) , \]  
(14)

we obtain

\[ \frac{d^2 w}{dz^2} + (2-z) \frac{dw}{dz} + \frac{\pi}{6} \left( 2 - e^{-i(z+2)} \right) \]  
(15)

The solutions of the complementary equation are the confluent hypergeometric functions \([11]\) \( M(-\frac{1}{3},2,z) \) and \( U(-\frac{1}{3},2,z) \) whence the general solution of (15) is

\[ w(z) = AM(-\frac{1}{3},2,z)+BU(-\frac{1}{3},2,z)+w_p(z) , \]  
(16)

where \( A \) and \( B \) are arbitrary constants and \( w_p \) is a particular integral of (15). Henceforth, we will abbreviate \( M(-\frac{1}{3},2,z) \) and \( U(-\frac{1}{3},2,z) \) to \( M(z) \) and \( U(z) \).

Of course, a physically reasonable \( w(z) \) must satisfy certain conditions. For example, although \( M(z) \) is finite for all \( z \), it grows asymptotically as \( z^{-8/3} e^{+z} \) and any solutions of (15) which increase this fast destroy the integrability of (3). Conversely, \( U(z) \) grows asymptotically only as \( z^{1/2} \) but is singular at \( z = 0 \). If we stipulate both that the integral (3) converge and that \( w(z) \) be finite everywhere, the constants \( A \) and \( B \) in (16) are determined and the resulting \( w(z) \) is therefore unique. Using the method of variation of parameters [12] to solve (15) and choosing the integration limits so that our stipulations are satisfied leads, after some simplification, to

\[ w(z) = \frac{1}{2} - \frac{1}{4} \Gamma(\frac{1}{3}) \left[ M(z) \int_0^z a(a+2)e^{-2a}U(a)da \right. 
\]  
\[ + U(z) \int_0^z a(a+2)e^{-2a}M(a)da \left. \right] . \]  
(17)

Using (17), we can compute the exchange energy of the hydrogen atom as

\[ E_x = -\int_0^\infty z^2 e^{-z} w(z) dz , \]  
(18)

Evaluating (18) numerically leads to \( E_x = -0.3125 \), which is the correct value.

Our progress to this point may be summarized as follows:

(a) Equation (17) corresponds to the unique exchange functional of the form (3), which is exact for the hydrogen atom.

(b) Because (3) is dimensionally consistent, the functional is also exact for all hydrogenlike ions (viz. \( He^+, Li^+, \ldots \)).

(c) Because (12) tends asymptotically to \(+1/r\), and because (11) and (12) are equal and opposite by construction, the functional necessarily has the correct \(-1/r\) asymptotic exchange potential.

Despite its unwieldy appearance, (17) simplifies for large values of \( z \). As \( z \) increases, the first integral in (17) decays exponentially while the second rapidly tends to a constant. Consequently,

\[ w(z) \approx \frac{1}{2} - 0.281 \ln 271 U(z) \]  
(19)

so that, for large \( z \),

\[ g(x) = O(x(\ln x)^{2/3}) . \]  
(20)

It is interesting to compare this with

\[ g(\text{Beck}) = O(x(\ln x)^{-1}) . \]  
(21)

The contrast between (20) and (21) is consistent with the observation by Ortiz and Balonne that the Becke functional does not provide the correct asymptotic behavior for the exchange potential [13].

\[ \text{FIG. 1. Functions } g(x) \text{ corresponding to Eqs. (5)--(7) and (14).} \]
similar estimates (−0.2680, −0.3010, −0.3095, and −0.3125 hartrees, respectively) of the exchange energy.

We are now led to ask how well the new functional works for larger atoms. For helium, it gives an energy which is about 2 mhartrees higher than the Hartree-Fock (HF) energy but, for still larger atoms, it greatly overestimates the exchange energy (and hence the total energy). The resulting energies of the nitrogen and neon atoms, respectively, are −57.5 and −136.3 hartrees, which are each several hartrees below their HF values. That a functional which is exact for the hydrogen atom gives the wrong answers for larger atoms incidentally proves that the “universal” exchange functional cannot be expressed in the form (3).

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[10] It should be noted that the term “exact” used here implies that, if the Kohn-Sham equation for the hydrogen atom is solved with this exchange functional, the resulting energy and atomic orbital will be precisely those obtained by solving the Schrödinger equation exactly.