Introduction to Density Functional Theory: Calculations by Hand on the Helium Atom

Kyle A. Baseden and Jesse W. Tye*

Department of Chemistry, Ball State University, Muncie, Indiana 47306, United States

S *Supporting Information*

ABSTRACT: Density functional theory (DFT) is a type of electronic structure calculation that has rapidly gained popularity. In this article, we provide a step-by-step demonstration of a DFT calculation by hand on the helium atom using Slater's X-Alpha exchange functional on a single Gaussian-type orbital to represent the atomic wave function. This DFT calculation is compared and contrasted with a Hartree–Fock calculation on the same system. This information is accessible by advanced undergraduate students studying physical chemistry or calculus-based physics.

KEYWORDS: *Upper-Division Undergraduate, Graduate Education/Research, Physical Chemistry, Calculator-Based Learning, Computer-Based Learning, Hands-On Learning/Manipulatives, Theoretical Chemistry, Molecular Modeling, Computational Chemistry, Laboratory Computing/Interfacing*

■ INTRODUCTION

Electronic structure calculations serve an important role in the understanding of chemical structure and reactivity. The release of user-friendly, commercial electronic structure programs has led to increased access to the techniques of computational chemistry by undergraduate students. Unfortunately, these programs have been both a boon and a curse to the understanding of electronic structure theories by students. The programs have become so easy to use that novice users may misuse and overextrapolate the output of these programs. Novice chemists may not appreciate that fact that approximate computations can give useful insight into experimental results if you understand what a particular computation tells you and what it does not.

Density functional theory (DFT) is a type of electronic structure calculation that continues to gain popularity. A deep understanding of DFT is possible for junior and senior undergraduates in physical chemistry courses as well as beginning graduate students. To the best of our knowledge, all modern physical,[1] quantum,[2] and computational[3] chemistry texts lack clear illustration of the implementation of density functional theory by specific examples. In general, quantum concepts are best understood by examining the full treatment of simple systems by hand. This technique can give clear insight into the manner in which the theory is implemented in programs. This Journal has published a number of articles that give step-by-step details of Hartree–Fock calculations on small atoms and molecules[4] as well as articles on a range of other aspects of computational chemistry.[5]

Some important types of modern calculations are Hartree–Fock (HF), Møller–Plesset perturbation theory (MP) and configuration interaction (CI), and density functional theory (DFT) calculations.[2,6] The main practical difficulty for all electronic structure theories is the proper treatment of electron–electron interactions in species that contain two or more electrons. HF, MP, and CI calculations rely on the computation of the atomic or molecular wave function, whereas DFT requires computation of the total electron density and technically does not require a wave function. In practice, however, DFT generally uses a wave function to compute some parts of the energy and the electron density to compute other parts of the energy. The total electron density and the normalized wave function can be interrelated because the total electron density is the absolute value of the square of the normalized wave function divided by the number of electrons. Hartree–Fock treats the electron–electron interactions in a very approximate way and, therefore, is the least accurate of these four methods.

HF theory has a number of well-established shortcomings and this method alone is generally not accurate enough to study most chemical reactions.[3] MP and CI, which build upon the HF calculation, provide very accurate electronic energies for small atoms and molecules when using very large basis sets, but the methods are too computationally expensive to apply to larger atoms and molecules. Modern implementations of DFT can provide much higher accuracy than HF calculations at a lower computational cost. The low computational cost of DFT has led to a steady increase in the use of density functional theory for the study of larger molecules.[3,6]

Mathematical Functions and Functionals

An understanding of mathematical functions and functionals is required to understand the basic language of DFT. Functions take a number as input and yield a number as output. For example, eq 1, could take $x = 2$ as input and yield $f(x) = 4$ as output. Functionals are functions of functions. Functionals take a function as input and yield a number as output. The input for a function is enclosed in parentheses (for example $f(x)$),

whereas the input for a functional is enclosed in square brackets (for example $F[y]$). A very simple functional is the definite integral functional, $F[y]$ that yields the area under any provided function, y. For example, let us say that we are interested in the area under any general curve, $y = f(x)$, from $x = 0$ to $x = 3$. The functional, $F[y]$, is then given by eq 2

$$y = f(x) = 2x \tag{1}$$

$$F[y] = \int_0^3 f(x)\, dx \tag{2}$$

The functional $F[y]$ in eq 2 could take the function given in eq 1 as input and yield the output $F[2x] = 9$. Functionals can be defined as either local or nonlocal. A functional is local if the functional's value can be computed for small segments of the input curve and then summed to find the total value. Otherwise the functional is called nonlocal. A density functional takes the electron density (a function of the position coordinate, r) as an input and outputs a number (an energy). Density functionals can be local or nonlocal.

Components of the Total Electronic Energy

It is often useful to partition the total electronic energy of an atom, molecule, or ion, E_{tot}, into the components shown in eq 3, where E_T is the total kinetic energy of the electrons, E_v is the total potential energy of the electrons due to their Coulombic attraction to the nuclear center(s), E_J is the total potential energy due to the average Coulomb repulsion between pairs of electrons, E_X is the total quantum mechanical exchange energy of the electrons, and E_c is the total correlation energy of the electrons[7]

$$E_{tot} = E_T + E_V + E_J + E_X + E_C \tag{3}$$

The E_X and E_C terms correct for the overly simplistic E_J term, which is based on the average repulsion between electrons. The E_J term does not take into account the correlated motion of electrons. The electrons in an atom or molecule constantly and instantaneously adjust to avoid one another. The larger E_X term corrects for the strongly correlated motion of electrons of the same spin and removes nonphysical self-repulsion terms in E_J. The smaller E_C term mainly corrects for the more weakly correlated motion of electrons of opposite spin. The E_T and E_J terms are always positive, whereas the E_V, E_X, and E_C terms are always negative. The calculation of the E_T, E_V, and E_J terms are identical in many implementations of Hartree–Fock and density functional theory. The E_X term is calculated differently in HF and DFT. The E_C term is completely missing in HF theory but can be included in an approximate way in DFT. The correlation energy is due to the ability of all of the electrons in an atom or molecule to adjust to avoid the other electrons and it may be defined mathematically as the difference between the exact nonrelativistic energy and the Hartree–Fock energy. The Hartree–Fock limit is the most accurate energy attainable without considering electron correlation.

Beginnings of Density Functional Theory

Schrödinger published his famous equation that predicts behavior of particles in a quantum system in 1926.[8] The Schrödinger equation is a partial differential equation that shows how a quantum system evolves over time. The central idea of Schrödinger's theory is that all of the information about a quantum system is contained in the system's wave function. At the very least, Schrödinger's wave function is a convenient mathematical construct that can used to calculate the total

energy and other properties of atoms and molecules. The meaning of the wave function has been debated since its inception, since the wave function is not directly observable by experiment. The wave function is the fundamental variable in Hartree–Fock and post-Hartree–Fock calculations. In 1927, Max Born interpreted the wave function in a probabilistic manner. Born showed the probability density determined by squaring the absolute value of the amplitude of a wave function yields the probability of the occurrence of a quantum event.[9]

Llewellyn Thomas and Enrico Fermi independently published atomic calculations that did not require a wave function but instead used the electron density as the fundamental variable in Thomas–Fermi (TF) theory in 1927.[10−12] Thomas and Fermi made a leap of faith in assuming from the outset that the total electronic energy of an atom or molecule is a functional of the electron density, although they never formally proved the existence of such a functional. One attractive feature of the electron density is that is it experimentally observable, unlike Schrödinger's wave function. The original Thomas–Fermi model included terms to compute the kinetic energy of the electrons (E_T), the potential energy due to electron–nuclear attraction (E_V), and the potential energy due to electron–electron repulsion (E_J) from the electron density. The TF model yields poor quantitative predictions for real atoms and molecules, because it is exact only in the limit of an infinite nuclear charge. It most glaring failures are its inability to compute the shell structure of atoms and the fact that it predicts that all molecules are less stable than their constituent atoms.[7] Because it considers the total energy to be a functional of the electron density, the Thomas–Fermi energy functional can be considered a forerunner to modern DFT. The TF kinetic energy functional produced errors of around 10% in the calculated kinetic energy.[7] Over time, several improvements were made to the original TF functional. In 1930, Paul Dirac[13] added a term to describe the exchange energy of the electrons (E_X), and in 1935, Carl Friedrich von Weizsäcker[14] added correction term for the kinetic energy of the electrons (Weizsäcker correction).[7] Even with the additional terms added by Dirac and von Weizsäcker the TF functional still yields a bad estimate of total energy and fails to predict the shell structure of atoms.[7] In 1950, J. C. Slater derived an exchange functional by dimensional analysis that only differed from Dirac's by a multiplicative constant.[7,15]

Modern DFT has its roots in the work of Pierre Hohenberg, Walter Kohn, and Lu Jeu Sham. Hohenberg and Kohn showed that a universal functional for the total electronic energy of an atom, molecule, or ion, $E_{tot}[n(r)]$, can be defined in terms of the electron density, $n(r)$, and showed that the total electronic energy and other observable properties are a functional of $n(r)$.[16] They further proved that the input of the exact ground state electron density into this universal functional yields the global minimum value of this energy functional.[17] Although the work of Hohenberg and Kohn proved that the universal density functional must exist, their work does not prescribe the form for this functional nor the way in which the electron density should be described. The total electronic energy can be written as shown in eq 4, where each term is dependent on the total electron density, $n(r)$. The equation developed by Kohn and Sham made DFT a practical computational tool.[18] The Kohn–Sham equation is the Schrödinger equation of a fictitious system of noninteracting electrons that generate the same density as the system of interest. This approximation allowed Kohn and Sham to more accurately compute each electron's

2117

dx.doi.org/10.1021/ed5004788 | J. Chem. Educ. 2014, 91, 2116−2123

kinetic energy in terms of Kohn—Sham orbitals in a manner analogous to HF

$$E_{\text{tot}}[n] = E_T[n] + E_V[n] + E_J[n] + E_X[n] + E_C[n] \quad (4)$$

The electron density can be represented using different several types of mathematical functions.[3] The original DFT calculations were performed using planewave functions as basis sets. The infinite extent of these functions was ideal for computations on extended structures such as metal surfaces or crystalline solids. For calculations of discrete atoms and molecules, atom-centered basis sets are generally more appropriate. In this text, the electron density is represented by a single atom-centered Gaussian basis function, $\chi_i(r)$. In general, the optimization of the total electron density, $n(r)$, is accomplished by systematic variation of the linear expansion coefficients, c_i, in eq 5 to obtain the lowest possible total energy

$$n(r) = \left(\sum_{i=1}^{x} (c_i \chi_i(r)) \right)^2 \quad (5)$$

■ STRENGTHS AND WEAKNESSES OF OUR MODEL

We have chosen to use the Kohn—Sham formulation of DFT to compute the total energy of the helium atom, because helium's total energy is accurately known from experiment. The experimentally observed total electronic energy of the helium atom is −2.9034 au.[19] The total electronic energy of the He atom is determined as the sum of the first and second ionization energies.

$$\varphi(r) = 2\left(\frac{2\alpha_{\text{orb}}}{\pi} \right)^{3/4} \exp(-\alpha_{\text{orb}} r^2) \quad (6)$$

A variety of computational methods have been used in the past to calculate the total energy of the helium atom to very high accuracy.[20] Although our computations are not very accurate, they highlight many of the procedures used in higher-level computations and demonstrate the manner in which more accurate results may be obtained. We will discuss the shortcomings of our model. We have represented the 1s orbital of helium with a single normalized Gaussian type orbital (GTO, shown in eq 6). GTO's are the most common type of orbitals used in electronic structure calculations. The orbital exponent coefficient, α_{orb}, determines the rate at which the wave function and the electron density decrease as a function of increasing distance from an atomic center.[21] A single GTO is a poor model for the true atomic wave function of helium and its electron density. We expect that it will yield poor values for the total electronic energy. The benefit to using a single GTO in our derivation is that it allows one to analytically integrate the exchange functional. The sole method of electron density variation and optimization in our calculation is adjustment of the orbital exponent coefficient, α_{orb}. In general practice, computations involve orbitals constructed from a linear combination of two or more GTO's in which the orbital exponent coefficients remain constant, and the linear expansion coefficients are optimized. The use of two or more GTO's would require us to use numerical integration of the exchange functional, and we find utility in being able to solve these equations analytically. We have chosen to model the exchange energy, E_X, using the Slater's X-Alpha exchange functional and to model correlation energy, E_C, we will use correlation functional (III) from Vosko, Wilk, and Nusair's paper.[22] All of

the calculations use atomic units, meaning that distances will be measured in units of the Bohr radius (a_0 = 52.9 pm) and energies are in units of hartree (or au = atomic units). Additional activities, including the calculation of the Hartree—Fock and X-Alpha atomic orbital energies, are given in the Supporting Information.

■ CLOSED-SHELL HARTREE—FOCK EQUATIONS

Let us first discuss a simple HF calculation first since the concept of the exchange energy originated in Hartree—Fock theory. Equation 7 is the HF equation for computing the total Hartree—Fock energy, $E_{\text{tot}}^{\text{HF}}$ for any closed-shell system of N electrons.[23] For the helium atom ($N = 2$), the general HF equation given in eq 7 greatly simplifies to yield eq 8.

$$E_{\text{tot}}^{\text{HF}} = 2 \sum_{a=1}^{N/2} h_{aa} + \sum_{a=1}^{N/2} \sum_{b=1}^{N/2} (2J_{ab} - K_{ab}) \quad (7)$$

$$E_{\text{tot}}^{\text{HF}}(\text{He}) = 2h_{11} + 2J_{11} - K_{11} \quad (8)$$

The equations consist of some terms that deal with one electron at a time and other terms that deal with two electrons at a time. The one-electron terms are the kinetic energy of each electron (T_{aa}) and the Coulombic potential energy of each electron due to its attraction by the nuclei (V_{aa}). The T_{aa} and V_{aa} terms for each electron are generally summed together to yield a single one-electron term for each electron called the core term, h_{aa}. The J_{ab} and K_{ab} terms are the two-electron terms. The J_{ab} terms are the electron—electron Coulomb repulsion energy terms. These terms are due to the Coulombic potential energy of the repulsion of each electron with every electron in the system (including itself). The K_{ab} terms are exchange energy terms. These terms are due to the exchange interaction of each electron with every electron in the system with the same spin (including itself). The K_{ab} terms are a consequence of the antisymmetric nature of the wave functions used for these calculations. The two-electron J_{ab} and K_{ab} terms change during the optimization of the wave function, whereas the one-electron h_{aa} terms remain constant.

The number of Coulomb and expected exchanged interactions is easy to illustrate diagrammatically as shown in Figure 1
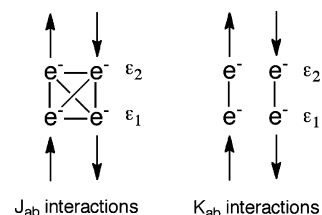

Figure 1. Simple diagram showing the J_{ab} interactions between all electrons and K_{ab} interactions between electrons of the same spin. ε_1 and ε_2 are the names of the orbitals containing these electron pairs.

for a closed-shell 4-electron system. For this system, one expects six J_{ab} terms among the four electrons and one K_{ab} between the two up electrons and one K_{ab} term between the two down electrons. One can generalize to say that one expects N-electron system to experience $((N(N-1))/2)$ Coulomb interactions and $((N(N-2))/8)$ exchange interactions between the up electrons $((N(N-2))/8)$ between the down electrons. Interestingly, the J_{ab} and K_{ab} summations in eq 7 lead to more Coulomb and exchange terms than one

would expect. For an N-electron system, eq 7 predicts $N^2/2$ Coulomb interactions and $N^2/4$ total exchange interactions. The $N/2$ extra J_{aa} terms are referred to as self-repulsion interactions and the $N/2$ extra K_{aa} terms are referred to as a self-exchange interactions. In HFT, the J_{aa} and K_{aa} terms are equal in magnitude (for the same a), and therefore, the self-repulsion term is completely removed by the self-exchange term.

Calculation of the T, V, J, and K Energy Terms

Thijssen's text gives the necessary equations for the calculation of the one-electron T_{ab} and V_{ab} terms that compose h_{ab} as well as the two-electron J_{ab} and K_{ab} terms involving multiple 1s GTO's on multiple atomic centers.[24] We have simplified the equations given in Thijssen's text since we are dealing with a single normalized GTO located on a single helium center ($Z = 2$ for the V term) and these are given as eqs 9−12 below.

$$h_{11} = T_{11} + V_{11} \tag{9}$$

$$T_{11} = \left\langle \varphi_1 \left| \frac{1}{2} \nabla^2 \right| \varphi_1 \right\rangle = +1.5(\alpha_{\text{orb}}) \tag{10}$$

$$V_{11} = \left\langle \varphi_1 \left| \frac{2}{r} \right| \varphi_1 \right\rangle$$
$$= -\left(\frac{32}{\pi} \right)^{1/2} (\alpha_{\text{orb}})^{1/2}$$
$$\approx -3.192(\alpha_{\text{orb}})^{1/2} \tag{11}$$

$$J_{11} = K_{11}$$
$$= \left\langle \varphi_1 \varphi_1 \left| \frac{1}{r} \right| \varphi_1 \varphi_1 \right\rangle$$
$$= \left(\frac{4}{\pi} \right)^{1/2} (\alpha_{\text{orb}})^{1/2}$$
$$\approx +1.128(\alpha_{\text{orb}})^{1/2} \tag{12}$$

■ CLOSED-SHELL DFT EQUATIONS

The closed shell DFT equations for an N-electron system are simple to derive from the corresponding closed-shell HF equations. The sum of K_{ab} terms in the HF equation for the total electronic energy is replaced by the total exchange energy term, E_X, to yield the DFT computed total electronic energy, $E_{\text{tot}}^{\text{DFT}}$ as shown in eq 13. The summations in eq 13 are over one term since helium is a two-electron system ($N = 2$). The general DFT equations given in eq 13 greatly simply to yield eq 14

$$E_{\text{tot}}^{\text{DFT}} = 2 \sum_{a=1}^{N/2} h_{aa} + \sum_{a=1}^{N/2} \sum_{b=1}^{N/2} (2J_{ab}) - E_x \tag{13}$$

$$E_{\text{tot}}^{\text{DFT}}(\text{He}) = 2h_{11} + 2J_{11} - E_x \tag{14}$$

In DFT, the J_{ab} terms are calculated in the same manner as HFT, but the sum of K_{ab} terms is approximated by an E_X term using an approximate density functional. Because the E_X term in DFT calculations is approximate, it may not completely remove the energy from self-repulsion J_{aa} terms. Therefore, DFT computed energies may reflect some unremoved self-repulsion energy.

Homogeneous Electron Gas

The exchange and correlation energy density functionals can only be determined accurately for very simple model systems.

The homogeneous electron gas (HEG, also known as the uniform electron gas or jellium) is an important theoretical construct that bears discussion before proceeding further. One can imagine constructing the HEG by placing N electrons and a uniformly distributed total positive charge of N^+ into a cube of volume, V, so that the net charge within the cube is zero. The electrons within this cube maintain a uniform electron density since the positive charge is uniformly distributed within the cube rather than concentrated in nuclei. The potential energy of attractions between the electrons and the homogeneous positive charge (E_V) exactly cancels potential energy due to the electron−electron repulsions (E_J). Therefore, the total energy of the HEG is simply the sum of the total kinetic energy (E_T), total exchange energy (E_X), and total correlation energy (E_C).

The exchange energy per electron for the homogeneous electron gas was calculated analytically by Bloch[25] (in 1929) and Dirac[13] (in 1930) using planewave basis functions.[26,27] The equation for the Hartree−Fock exchange energy can be rewritten as a functional of the first order density matrix, which can be approximated as the sum of the squares of the $N/2$ occupied orbitals. In the limit of $N \to \infty$, $V \to \infty$ with N/V remaining finite, the sum of over $N/2$ occupied orbitals is replaced by integration over a sphere from 0 to $k_F = (3\pi^2 n(r))^{1/3}$, where k_F is the wavevector of the highest occupied orbital in our system known as Fermi wavevector. Following some tedious math, this result yields the exchange energy per electron for the HEG.

Local Density Approximation Exchange Functional

The simplest exchange functional is referred to as the local density approximation (LDA) functional for closed-shell systems. The LDA exchange functional is based on the assumption that the exchange energy density at every position in space for an atom or molecule can be modeled as the exchange energy density of the HEG having the *same* density that is found at that position. To be entirely clear, invoking the uniform electron gas as the source of the exchange energy functional is <u>not</u> equivalent to assuming that the electron density of the *atom or molecule* is a constant throughout space.

The exchange energy per electron, $\varepsilon_X^{\text{HEG}}$, has been computed for the HEG and is given in eq 15. Because the total electron density is the number of electrons per unit volume, multiplication of $\varepsilon_X^{\text{HEG}}$ by the total electron density yields the exchange energy per unit volume (E_X/V). Integration over all space ($d\tau = 4\pi r^2 \, dr$ in spherical coordinates) yields the total exchange energy of the system, which is shown in eq 16. In this text, we will use Slater's X-Alpha functional[15] for calculation of the exchange energy. Slater's formulation of an exchange functional multiplies the LDA equations by an empirical scaling constant of 1.05 to yield the X-Alpha equations for the total exchange energy is given as eq 17

$$\varepsilon_X^{\text{HEG}}[n(r)] = -\left(\frac{3}{4} \right)\left(\frac{3}{\pi} \right)^{1/3} (n(r))^{1/3} \tag{15}$$

$$E_X^{\text{LDA}} = -(4\pi) \int_0^\infty (r^2)(\varepsilon_X^{\text{HEG}})(n(r)) \, dr$$
$$= -\left(\frac{3}{4} \right)\left(\frac{3}{\pi} \right)^{1/3} (4\pi) \int_0^\infty (r^2)(n(r))^{4/3} \, dr \tag{16}$$

$$E_X^{X\alpha} = -1.05\left(\frac{3}{4} \right)\left(\frac{3}{\pi} \right)^{1/3} (4\pi) \int_0^\infty (r^2)(\eta(r))^{4/3} \, dr \tag{17}$$

Correlation Functionals

There is no analytical expression for the correlation energy at the intermediate electron densities generally observed in atoms and molecules. The correlation energy per electron can be solved exactly at the limits of very low and very high electron density, but the expression for the intermediate electron densities present in atoms and molecules is unknown. In 1980, Ceperley and Alder performed accurate quantum Monte Carlo simulations on the HEG at intermediate densities.[28] Various researchers have proposed equations to estimate the correlation energy per electron at intermediate electron densities by extrapolation of the between the low density and high-density limits or based on the work of Ceperley and Alder.[6]

Calculation of the Total Electron Density and E_X

A normalized GTO for a 1s orbital was given in eq 6. The total electron density for this two-electron system is the absolute value of the GTO basis function squared then divided by N ($N = 2$ for He) to yield eq 18. The four-third root of $n(r)$ is easily computed from eq 18 and given in eq 19. The substitution of eq 19 into eq 17 yields a known definite integral.[29] The use of a table of integrals and simplification of the constants yields eq 20[30]

$$n(r) = 2\left(\frac{2\alpha_{\text{orb}}}{\pi}\right)^{3/2}\exp(-2\alpha_{\text{orb}}r^2) \tag{18}$$

$$n(r)^{4/3} = (2)^{4/3}\left(\frac{2\alpha_{\text{orb}}}{\pi}\right)^2\exp\left(-\frac{8}{3}\alpha_{\text{orb}}r^2\right) \tag{19}$$

$$E_X^{X\alpha} = -1.05\left(\frac{3^{17}}{2^{19}\pi^5}\right)^{1/6}(\alpha_{\text{orb}})^{1/2} \approx -1.013(\alpha_{\text{orb}})^{1/2} \tag{20}$$

■ CALCULATION OF THE TOTAL ELECTRONIC ENERGY

Using eqs 8, 14, and 9−12, eqs 21 and 22 can be written for the total energy of the helium atom as a function of the orbital coefficient, α_{orb}. The optimal values of α_{orb} yield the minimum total energy for Hartree−Fock and X-Alpha calculations using this basis set. The optimal value of α_{orb} for eqs 21 and 22 can be determined analytically by differentiation of these expressions with respect to α_{orb}. The optimal values for α_{orb} are 0.769 for the HF calculation and 0.734 for the X-Alpha calculation. Substitution of the optimal values into eqs 21 and 22 yield our computed values for the total electronic energy of the helium atom, E_{tot}, using each model. We compute values of $E_{\text{tot}}^{\text{HF}} = -2.3012$ au from the HF calculation and $E_{\text{tot}}^{X\alpha} = -2.2008$ au from the X-Alpha computation. The optimal α value is inversely related to the size of the orbital. The α value obtained for the X-Alpha computation is smaller because the unremoved self-repulsion causes the orbital to expand relative to the HF orbital

$$E_{\text{tot}}^{\text{HF}} = 2(1.5\alpha_{\text{orb}}) - 2(3.192(\alpha_{\text{orb}})^{1/2}) + 2(1.128(\alpha_{\text{orb}})^{1/2})$$
$$- 1.128(\alpha_{\text{orb}})^{1/2} \tag{21}$$

$$E_{\text{tot}}^{X\alpha} = 2(1.5\alpha_{\text{orb}}) - 2(3.192(\alpha_{\text{orb}})^{1/2}) + 2(1.128(\alpha_{\text{orb}})^{1/2})$$
$$- 1.013(\alpha_{\text{orb}})^{1/2} \tag{22}$$

Hartree−Fock and Exact Exchange

The term "exact exchange" is often misused or misunderstood in discussions of quantum chemistry. The Hartree−Fock exchange energy is the exact exchange energy for the single determinant wave function that yields the minimum total energy from the Hartree−Fock equation. It does not mean that the value of the Hartree−Fock exchange is the correct amount of exchange energy for an atom or molecule using any other theory. Some early attempts at calculating accurate total energies using DFT attempted to develop a correlation functional as an add-on for HF calculations. Those correlation functionals performed much more poorly when compared to experimental data than calculations in which both the exchange and correlation functionals had been developed in tandem. The central issue is that fact that the wave function has a different meaning in these two theories. The optimal wave function in HFT is the wave function that minimizes the HF total energy equation, whereas the wave function in DFT is the wave function that yields the density that minimizes the Kohn−Sham total energy equation.

In order to demonstrate the manner in which the different theories yield different wave functions, we performed a calculation in which we added the VWN correlation functional energy to a HF calculation of total energy of the helium atom using a single GTO, which we refer to as HFVWN. The value of α that minimizes the HFVWN total energy, $\alpha_{\text{opt}}^{\text{HFVWN}}$ is found to be 0.750, which yields a computed total energy of −2.4504 au. This value differs from the optimal value for the HF calculation, $\alpha_{\text{opt}}^{\text{HF}} = 0.769$. The different values of α yield different atomic wave functions, and therefore, the use of the HF exchange energy in this calculation has no theoretical basis.

Theory Effects and Basis Set Effects

We have calculated the total electronic energy for the helium atom using a single GTO by hand (entries 3 and 7 in Table 1)

Table 1. Comparison of Basis Sets and Methods for Calculation of the Total Electronic Energy and Atomic Orbital Energy of Helium[a]

entry	type of data	basis set	E_{tot}	% of HF limit
1	experiment	n/a	−2.9034	n/a
2	HF limit	n/a	−2.8617	n/a
3	HF	STO-1G	−2.3012	80
4	HF	STO-2G	−2.7022	94
5	HF	STO-3G	−2.8078	98
6	HF	STO-6G	−2.8463	99
7	X-Alpha	STO-1G	−2.2008	77
8	X-Alpha	STO-2G	−2.5960	91
9	X-Alpha	STO-3G	−2.7026	94
10	X-Alpha	STO-6G	−2.7413	96

[a]Equations 21 and 22 give values of -2.3021 and -2.2025 au for entries 3 and 7 due to rounding of constants.

as well by a series of computations using the Gaussian 09 program using different basis (entries 4−6 and 8−10).[31,32] Our single GTO basis set is not an accurate representation of the 1s wave function. Better basis sets can be built from a linear combination of GTO's. Entries 4−6 and 8−10 use STO-nG basis sets in which the 1s atomic orbital is represented by linear combination of n GTO basis functions.[3,33] It is obvious that the total energies calculated by either method rapidly improve as quality of the basis set increases. The comparison of entries 3−6 with entries 7−10 shows that in this case the value of total electronic energy is only slightly better for HF versus the X-Alpha method. The HF and X-Alpha computed values for the total electronic energy are shown to improve as the number of GTO basis functions is increased.[34]

Table 2. Computed[a] **Energy Components For Selected Closed-Shell Atoms**

atom	N	E_T	E_V	E_J	E_X	E_{tot}	%HF[b]	%SIC[c]
He	2	2.7	−6.5	2.1	−0.9	−2.6	90	100
Be	4	14.3	−33.1	7.6	−2.5	−13.6	91	50
Ne	10	121.5	−299.1	67.3	−11.7	−122.1	95	20
Ar	18	491.2	−1197.5	229.0	−28.8	−506.2	96	11
Kr	36	2741.2	−6558.8	1172.1	−93.0	−2738.4	99	6

[a]These results were calculated using the X-Alpha method as implemented in Gaussian 09 using the STO-2G basis set in each case. [b]Percent of HF exchange energy obtained from the X-Alpha using the same basis set. [c]Percent of exchange interactions due to self-exchange interactions. It is not the percentage of the total exchange energy due to self-exchange interactions.

Helium Is the Exception That Proves the Rule

Table 2 illustrates three reasons that the helium atom is the worst-case scenario for density functional theory: (1) The helium atom has the largest percent of exchange interactions due to self-exchange (100%). The percent of K_{ab} terms due to self-exchange for an N-electron system is $2/N \times 100\%$.[35] It is obvious that the fraction of K_{ab} interactions due to self-exchange rapidly decreases with increasing N. For example, only 20% of K_{ab} interactions are due to self-exchange for the neon atom ($N = 10$). (2) Self-exchange interactions are the largest K_{ab} terms. For example in the Be atom, the K_{1s1s} interaction was found to be three times larger than the K_{2s2s} interaction and 28.5 times larger than the K_{1s2s} interaction.[36] (3) The exchange energy is a larger portion of the total energy for the helium atom than for any other atom. As the nuclear charge and total number of electrons increases the E_T, E_V and E_J terms increase much more rapidly than the E_X term. Table 2 contains the results of X-Alpha calculations performed with the Gaussian 09 program utilizing the STO-2g basis set. Comparison of He ($N = 2$) and Kr ($N = 36$) in Table 2 shows that the E_T and E_V terms in Kr are more than 1000 times larger than in He, the E_J term in Kr is more than 500 times larger than in He, but the E_X term in Kr around 100 times larger than in He.

The moral of the story is that the DFT calculation is doing a pretty good job under horrible working conditions. Our calculation utilizing the smallest possible Gaussian basis set and the simplest exchange functional and being performed on the most difficult neutral atom in the periodic table yields 76% of the Hartree−Fock limit. X-Alpha calculations performed on the He atom with the Gaussian 09 program using the commonly used (but still small) 6-31g basis set yields 96% of the Hartree−Fock limit. DFT provides a much less computational intensive method to include the approximate exchange and correlation energy than wave function-based methods.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Optional activities related to calculation of the orbital energy, most probable radius, and effect of the nuclear charge in DFT and HF theories have been included. This material is available via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: jwtye@bsu.edu.

Notes

The authors declare no competing financial interest.

REFERENCES

(1) (a) Atkins, P.; de Paula, J. *Physical Chemistry*, 8th ed.; Freeman/Worth: New York, NY, 2007. (b) Berry, R. S. *Physical Chemistry*; John Wiley & Sons Inc.: Hoboken, NJ, 1980. (c) Cooksy, A. *Physical Chemistry: Quantum Chemistry and Molecular Interactions*; Prentice Hall: Upper Saddle River, NJ, 2013. (d) Engel, T. *Physical Chemistry*, 2nd ed.; Prentice Hall: Upper Saddle River, NJ, 2009. (e) Laidler, K. J.; Meiser, J. H.; Sanctuary, B. C. *Physical Chemistry*, 4th ed.; Cengage Learning: Independence, KY, 2002. (f) Levine, I. *Physical Chemistry*, 6th ed.; McGraw-Hill Science/Engineering/Math: New York, NY, 2008. (g) McQuarrie, D. A. *Physical Chemistry: A Molecular Approach*; University Science Books: Sausalito, CA, 1997. (h) McQuarrie, D. A.; Simon, J. D. *Physical Chemistry: A Chemical Approach*; University Science Books: Sausalito, CA, 1997. (i) Silbey, R. J.; Alberty, R. A.; Bawendi, M. G. *Physical Chemistry*, 4th ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2005.

(2) (a) Anderson, J. M. *Mathematics for Quantum Chemistry*; Dover Books on Chemistry; Dover Publications: Mineola, NY, 2005. (b) Atkins, P. W.; Friedman, R. S. *Molecular Quantum Mechanics*, 5th ed.; Oxford University Press: New York, NY, 2005. (c) Fitts, D. D. *Principles of Quantum Mechanics: As Applied to Chemistry and Chemical Physics*; Cambridge University Press: New York, NY, 1999. (d) Hanna, M. H. *Quantum Mechanics in Chemistry*, 3rd ed.; Physical Chemistry Textbook Series; Benjamin-Cummings Publishing Co.: San Francisco, CA, 1981. (e) House, J. E. *Fundamentals of Quantum Chemistry*, 2nd ed.; Complementary Science Series; Elsevier Academic Press: Burlington, MA, 2004. (f) Levine, I. N. *Quantum Chemistry*, 5th ed.; Prentice Hall: Upper Saddle River, NJ, 1999. (g) Lowe, J. P.; Peterson, K. *Quantum Chemistry*, 3rd ed.; Elsevier Academic Press: Burlington, MA, 2006. (h) Martin, R. M. *Electronic Structure: Basic Theory and Practical Methods*; Cambridge University Press: New York, NY, 2004. (i) McQuarrie, D. A. *Quantum Chemistry*, 2nd ed.; University Science Books: South Orange, NJ, 2007. (j) Schatz, G. C.; Ratner, M. A. *Quantum Mechanics in Chemistry*; Dover Books on Chemistry; Dover Publications: Mineola, NY, 2002. (k) Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*; Dover Books on Chemistry; Dover Publications: Mineola, NY, 1989.

(3) (a) Cramer, C. J. *Essentials of Computational Chemistry: Theories and Models*, 2nd ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2004. (b) Clark, T. *A Handbook of Computational Chemistry: A Practical Guide to Chemical Structure and Energy Calculations*; John Wiley & Sons Inc.: Hoboken, NJ, 1980. (c) Cook, D. B. *Handbook of Computational Quantum Chemistry*; Dover Books on Chemistry; Dover Publications: Mineola, NY, 2005. (d) Jensen, F. *Introduction to Computational Chemistry*; John Wiley & Sons Inc.: Hoboken, NJ, 2007. (e) Grant, G. H.; Richards, W. G. *Computational Chemistry*; Oxford Chemistry Primers; Oxford University Press: New York, NY, 1995. (f) Hinchliffe, A. *Molecular Modelling for Beginners*, 2nd ed.; John Wiley & Sons Ltd: West Sussex, United Kingdom, 2008. (g) Hinchliffe, A.

Modelling Molecular Structures, 2nd ed.; Wiley Series in Theoretical Chemistry; John Wiley & Sons Ltd: West Sussex, United Kingdom, 2000. (h) Höltje, H. G.; Sippl, W.; Rognan, D.; Folkers, G. *Molecular Modeling: Basic Principles and Applications*, 2nd ed.; Wiley-VCH Verlag GmbH: Weinham, Germany, 2003. (i) Leach, A. *Molecular Modelling: Principles and Applications*, 2nd ed.; Prentice Hall: Saddle River, NJ, 2001. (j) Kohanoff, J. *Electronic Structure Calculations for Solids and Molecules: Theory and Computational Methods*; Cambridge University Press: New York, NY, 2007. (k) Leszczynski,, J. *Handbook of Computational Chemistry*; Springer Reference/Springer: New York, NY, 2012. (l) Lewars, E. G. *Computational Chemistry: Introduction to the Theory and Applications of Molecular and Quantum Mechanics*; Kluwer Academic Publishers: Norwell, MA, 2003. (m) Martin, R. M. *Electronic Structure: Basic Theory and Practical Methods*; Cambridge University Press: New York, NY, 2004. (n) Rode, B. M.; Hofer, T. S.; Kugler, M. D. *The Basics of Theoretical and Computational Chemsitry*; Wiley-VCH Verlag GmbH: Weinheim, Germany, 2007. (o) Rogers, D. W. *Computational Chemistry Using the PC*, 3rd ed.; John Wiley & Sons Inc.: Hoboken, NJ, 2003. (p) Young, D. *Computational Chemistry: A Practical Guide for Applying Techniques to Real World Problems*; John Wiley & Sons Inc.: Hoboken, NJ, 2001.

(4) (a) Dewar, M. J. S.; Kelemen, J. LCAO MO theory illustrated by its application to H2. *J. Chem. Educ.* **1971**, *48*, 494−501. (b) Snow, R. L.; Bills, J. L. A simple illustration of the SCF-LCAO-MO Method. *J. Chem. Educ.* **1975**, *52*, 506−509. (c) Montomery, H. E. Helium Revisted: An introduction to variational perturbation theory. *J. Chem. Educ.* **1977**, *54*, 748−749. (d) Hoffman, G. G. An Excel file that performs SCF calculations on atoms. *J. Chem. Educ. (WebWare)* **2004**, 1−3. (e) Hoffman, G. G. Self-consistent field calculations on atoms using Excel. *J. Chem. Educ.* **2005**, *82*, 1418−1422. (f) Page, T. R.; Boots, C. A.; Freitag, M. A. Restricted Hartree-Fock calculations using Microsoft Excel. *J. Chem. Educ.* **2008**, *85*, 159. (g) Halpern, A. M.; Glendening, E. D. Exploring the Nature of the H$_2$ Bond. 1. Using Spreadsheet Calculations To Examine the Valence Bond and Molecular Orbital Method. *J. Chem. Educ.* **2013**, *90*, 1452−1458. (h) Halpern, A. M.; Glendening, E. D. Exploring the Nature of the H$_2$ Bond. 2. Using Ab Initio Molecular Orbital Calculations To Obtain the Molecular Constants. *J. Chem. Educ.* **2013**, *90*, 1459−1462.

(5) (a) Montgomery, H. E. Helium revisited: An introduction to variational perturbation theory. *J. Chem. Educ.* **1977**, *54*, 748−749. (b) Harriss, D. K.; Rioux, F. A simple Hartree SCF calculation on a one-dimensional model of the He atom. *J. Chem. Educ.* **1980**, *57*, 491−493. (c) Bills, J. L.; Snow, R. L. Orbital polarization by electron repulsion. *J. Chem. Educ.* **1982**, *59*, 142−144. (d) Moore, B. G.; Mize, J. D. Teaching theoretical physical chemistry: Density functional theory and the Taylor expansion of the van der Waals free energy. *J. Chem. Educ.* **1998**, *75*, 858. (e) Messina, M. The Hartree-Fock self-consistent field: An allegorical connection using two coupled harmonic oscillators. *J. Chem. Educ.* **1999**, *76*, 1439−1443. (f) Summerfield, J. H.; Beltrame, G. S.; Loeser, J. G. A simple model for understanding electron correlation methods. *J. Chem. Educ.* **1999**, *76*, 1430−1438. (g) Moore, B. G. Orbital plots using gnuplot. *J. Chem. Educ.* **2000**, *77*, 785−789. (h) Chattaraj, P. K.; Maiti, B. Electronic structure principles and atomic shell structure. *J. Chem. Educ.* **2001**, *78*, 811−813. (i) Matta, C. F.; Gillespie, R. J. Understanding and interpreting molecular electron density distributions. *J. Chem. Educ.* **2002**, *79*, 1141−1152. (j) Watson, L. A.; Eisenstein, O. Entropy explained: The origin of some simple trends. *J. Chem. Educ.* **2002**, *79*, 1269−1277. (k) Streit, B. R.; Geiger, D. K. Structure and bonding in group 14 congeners of ethene: DFT calculations in the inorganic chemistry laboratory. *J. Chem. Educ.* **2005**, *82*, 111−115. (l) Matito, E.; Duran, M.; Solà, M. A novel exploration of the Hartree-Fock homolytic bond dissociation problem in the hydrogen molecule by means of electron localization measures. *J. Chem. Educ.* **2006**, *83*, 1243−1248. (m) Waas, J. R. Semiempirical and DFT investigations of the dissociation of alkyl halides. *J. Chem. Educ.* **2006**, *83*, 1017−1021. (n) Bell, S.; Dines, T. J. Computational chemistry using modern electronic structure methods. *J. Chem. Educ.* **2007**, *84*, 1364−1370. (o) Simeon, T.; Aikens, C. M.; Tejerina, B.; Schatz, G. C. Northwestern university initiative for

teaching nanosciences (NUITNS): An approach for teaching computational chemistry to engineering undergraduate students. *J. Chem. Educ.* **2011**, *88*, 1079−1084. (p) Autschbach, J. Orbitals: Some fiction and some facts. *J. Chem. Educ.* **2012**, *89*, 1032−1040. (q) Zúñiga, J.; Bastida, A.; Requena, A. Using the screened coulomb potential to illustrate the variational method. *J. Chem. Educ.* **2012**, *90*, 1152−1158. (r) Montgomery, C. D. A mechanistic studt of the migratory insertion reaction: a computational chemistry exercise. *J. Chem. Educ.* **2013**, *89*, 1396−1400.

(6) (a) Politizer, P.; Seminario, J. M. *Modern Density Functional Theory: A Tool for Chemistry*; Elsevier: Amsterdam, The Netherlands, 1995. (b) Fiohais, C.; Nogueira, F.; Marques, M. A. L. *A Primer in Density Functional Theory*; Fiolhais, C., Nogueira, F., Marques, M. A. L., Eds.; Springer-Verlag: New York, NY, 2003. (c) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*, 2nd ed.; Wiley-VCH Verlag GmbH: Weinheim, Germany, 2002. (d) Parr, R. G.; Weitao, Y. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, NY, 1989. (e) Sholl, D.; Steckel, J. A. *Density Functional Theory: A Practical Introduction*; John Wiley & Sons, Inc.: Hoboken, NJ, 2009.

(7) Gill, P. M. W. Density functional theory (DFT), Hartree−Fock (HF), and the self-consistent field. In Encyclopedia of Computational Chemistry, Vol. *1*, Schleyer, P. v R., Ed. John Wiley and Sons: Chichester, U.K.,(1998) pp 678−689.

(8) Schrödinger, E. An Undulatory Theory of the Mechanics of Atoms and Molecules. *Phys. Rev.* **1926**, *28*, 1049−1070.

(9) Born, M. Zur Quantenmechanik der Stoßvorgänge. *Z. Phys.* **1926**, *37*, 863−867.

(10) Thomas, L. H. The calculation of atomic fields. *Math. Proc. Cambridge Philos. Soc.* **1927**, *23*, 542−548.

(11) Thomas and Fermi assume the total energy is a functional of the electron density, but do not formally prove the existence of such as functional.

(12) (a) Fermi, E. Un metodo statistico per la determinazione di alcune proprietà dell'atome. *Rend. Accad. Naz. Lincei* **1927**, *6*, 602. (b) Fermi, E. Eine statistische Methode zur Bestimmung einiger Eigenschaften des Atoms und ihre Anwendung auf die Theorie des periodischen Systems der Elemente. *Z. Phys.* **1928**, *48*, 73.

(13) Dirac, P. A. M. Note on Exchange Phenomena in the Thomas Atom. *Math. Proc. Cambridge Philos. Soc.* **1930**, *26*, 376−385.

(14) Weizsäcker, C. F. v. Zur Theorie der Kernmassen. *Z. Phys.* **1935**, *96*, 431−458.

(15) Slater, J. C. A Simplification of the Hartree-Fock Method. *Phys. Rev.* **1951**, *81*, 385−390.

(16) Hohenberg, P.; Walter, K. Inhomogeneous electron gas. *Phys. Rev.* **1964**, *136*, B864−B871.

(17) The electron density is also referred to as the number density (probable number of electrons per unit volume) or charge density (probable amount of electric charge per unit volume in units of −e).

(18) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, A1133−A1138.

(19) (a) Huheey, J. E. Keiter, E. A.; Keiter, R. L. *in Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; HarperCollins: New York, 1993. (b) James, A. M.; Lord, M. P. In *Macmillan's Chemical and Physical Data*; Macmillan, London, U.K., 1992.

(20) Drake, G. W. F. High Precision Theory of Atomic Helium. *Phys. Scr.* **1999**, *T83*, 83−92.

(21) The orbital exponent coefficient is often represented as simply α. We have chosen to represent it as α_{orb} in these equations to clearly distinguish it from Slater's scaling factor in the X-Alpha method.

(22) Vosko, S. H.; Wilk, L.; Nusair, M. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: A critical analysis. *Can. J. Phys.* **1980**, *58*, 1200−1211.

(23) Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*; Dover Books on Chemistry/Dover Publications: Mineola, NY, 1989.

(24) Thijssen, J. *Computational Physics*, 2nd ed.; Cambridge University Press: New York, NY, 2007.

(25) Bloch, F. Bemerkung zur Elektronentheorie des Ferromagnetismus und der elektrischen Leitfähigkeit. *Z. Phys.* **1929**, *57*, 545−555.

(26) Scuseria, G. E.; Staroverov, V. N. Progress in the development of exchange-correlation functionals. In *Theory and Applications of Computational Chemistry: The First Forty Years*, 1st ed.; Elsevier Science: Amsterdam, 2005; Chapter 24, pp 669−724.

(27) These planewave functions may be determined as the wave functions from the problem of three-dimensional fermions in a box. The wave functions of electrons in extended systems such as the HEG are best modeled as planewaves that have an infinite spatial extent rather than the atom centered basis sets normally used for discrete atoms, molecules, and ions.

(28) Ceperley, D. M.; Alder, B. J. Ground State of the Electron Gas by a Stochastic Method. *Phys. Rev. Lett.* **1980**, *45*, 566−569.

(29) Zwillinger, D. *Table of Integrals, Series, and Products*, 8th ed; Academic Press: Waltham, MA, 2014.

(30) The integral has the general form: $\int_0^\infty x^2 \exp(-cx^2)\, \mathrm{d}x = \frac{1}{4}\left(\frac{\pi}{c^3}\right)^{1/2}$

(31) Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*; Gaussian, Inc.: Wallingford, CT, 2009.

(32) The following series of IOp keywords are required in the input file in order for Gaussian 09 to print all of the relevant information: IOp(5/33=4), IOp(6/7=3), IOp(3/33=1), IOp(6/9=3), IOp(6/81=3).

(33) Slater-type orbital (STOs) resemble atomic orbitals more closely than the Gaussian-type orbitals (GTOs); however, calculations using STO's are much more computationally intensive than calculations using STOs. As a compromise, John Pople, used a linear combinations of n GTO's to approximate an STO. The n value in the STO-nG name describes the number of GTO's used. The quality of the basis set increases with increasing n value.

(34) The computed total energy from the HF calculation is converging toward the HF limit as the number of Gaussian functions in the basis set size is increased. The DFT-calculated total energy would converge to the experimental value as the basis set increases, if the exact density functional was used. Because X-Alpha is an approximate density functional, the computed total energy from the X-Alpha will converge toward a numerical value for each atom or molecule as the basis set is increased, but this value does not have a well-defined or physically meaningful limit.

(35) The fraction of self-exchange interactions is the number of self-exchange interactions divided by the total number of exchange interactions. Mathematically, it corresponds to $N/2$ self-exchange interactions divided by $N^2/4$ total exchange interactions to yield $2/N$ as the fraction of exchange interactions. To be clear, this value indicates the fraction of self-exchange interactions. It does not indicate the fraction of the exchange energy due to self-exchange interactions.

(36) Fischer, C. F. *The Hartree-Fock Method for Atoms: A Numerical Approach*; John Wiley & Sons Inc: Chichester, U.K., 1977; pp 236−237.