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The Minnesota Density Functionals and their Applications to Problems in Mineralogy and Geochemistry

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INTRODUCTION

Quantum mechanical electronic structure calculations are playing an increasingly useful role in many areas of mineralogy and geochemistry. This review introduces the density functional method for such calculations, gives an overview of the density functionals developed at the University of Minnesota, and summarizes selected applications using these density functionals that are relevant to mineralogy and geochemistry.

A key reason for the importance of computational methods in mineralogy is the ability to explore problems that cannot easily be studied in the laboratory. For example, it is very difficult to carry out laboratory studies under the real conditions of the Earth's mantle and core because the temperature of the Earth's core ranges up to 6000 K, and the pressure ranges up to 360 GPa. In the past decade, applications of quantum mechanical methods to understanding the properties of minerals and melts in the Earth's interior have become increasingly important (Warren and Ackland 1996; Oganov and Brodholt 2000; Stixrude and Peacor 2002; Brodholt and Vocadlo 2006; Gillan et al. 2006; Tsuchiya et al. 2006). Some specific examples of problems in solid-state geochemistry where electronic structure calculations can be particularly useful are phase equilibria (Tsuchiya et al. 2004; Lay et al. 2005; Schwegler et al. 2008), equations of state, elastic constants, bulk and shear moduli (Li et al. 2006), hydrogen, proton, and water diffusion in minerals (Sakamura et al. 2003; Belonoshko et al. 2004; Pöhlmann et al. 2004), the character and structural properties of hydroxyl groups in minerals and structures of hydrous minerals (Winkler et al. 1994, 1995; Nobes et al. 2000; Brodholt and Refson 2000; Churakov et al. 2003; Walker et al. 2006; Ockwig et al. 2009), hydrolysis and dissolution mechanisms (Strandh et al. 1997, Criscenti et al. 2006; Nangia and Garrison 2008; Morrow et al. 2009), and mineral fractionation (Blanchard et al. 2009).

In the field of geochemistry more broadly, computational quantum mechanics can also be very useful for understanding planetary hydrospheres and atmospheres (Andino et al. 1996; Tossell 2006; Qu et al. 2006; Kuwata et al. 2007; Hegg and Baker 2009; Gao et al. 2009) and oxidation-reduction mechanisms (Neal et al. 2003; Jaque 2007; Kwon et al. 2009) and for

determining the properties of metal nanoparticles and other nanominerals, whose importance in geologic materials is increasingly recognized (Reich et al. 2006; Hochella et al. 2008).

Most of the computational studies in all of these areas have employed Kohn-Sham density functional theory (KSDFT) (Kohn and Sham 1965; Kohn et al. 1996), which is the most popular electronic structure theory in solid-state physics and quantum chemistry. The next section of this review presents an introduction to KSDFT.

DENSITY FUNCTIONALS

KSDFT implicitly begins with the Born-Oppenheimer approximation (Born and Huang 1954; Mead 1988) in which the forces governing atomic motions (that is, internuclear motions, also called nuclear motions) are the negative gradient of a potential energy function that equals the sum of the electronic energy and the nuclear repulsion, and the electronic energy is the ground-state expectation value of the electronic Hamiltonian with the nuclei frozen in position. (Thus the usual potential energy function for nuclear motion is associated with the lowest eigenvalue of the electronic Hamiltonian; higher eigenvalues correspond to electronically excited states and may be calculated for optical spectroscopy or photochemistry.) The Born-Oppenheimer approximation provides a separation of electronic and nuclear motion, and it is expected to be very accurate for most problems in mineralogy and geochemistry, with the main exception being geochemical photochemistry. For the problems where the Born-Oppenheimer separation is valid, the key problem in attaining accurate computations is to make the calculated electronic energy accurate.

To find the electronic energy, KSDFT defines a reference Slater determinant (a Slater determinant is an antisymmetrized product of spin orbitals, where each spin orbital is usually taken as a product of a spin-up or spin-down spin function and a spatial orbital). The spin-up and spin-down electronic densities (which are called the spin densities) associated with this determinant (or, more generally, the spin density matrix associated with it) are the same as the exact spin densities (or space-spin density matrix) (Kohn and Sham 1965; von Barth and Hedin 1972). The electronic energy is given by the sum of the electron-nuclear attraction (and the electron interaction with any other external potential), the classical Coulomb energy of the electron density, and a universal functional of the density. In KSDFT this universal functional is separated into the reference-determinant electronic kinetic energy and an exchange-correlation energy, E_{XC}, which is a functional of the spin densities (or the space-spin density matrix). It is this (unknown) exchange-correlation functional that is usually called the density functional. The spin orbitals are determined by effective potentials computed as functional derivatives of the exchange-correlation energy per electron; this effective potential is discussed further below.

Although KSDFT is an exact many-body theory for the ground-electronic-state properties of systems such as atoms, molecules, surfaces, clusters, nanoparticles, amorphous solids, and crystals, it depends on a universal exchange-correlation functional that is unknown and can only be approximated. The accuracy of a KSDFT calculation depends on the quality of this approximated density functional. In placing KSDFT in context, we note that it differs in approach from the older method of seeking better and better approximations to the many-electron wave function, an approach now known as wave function theory (WFT). Accurate WFT calculations become expensive more rapidly with increasing system size than does KSDFT. Both KSDFT and WFT are in principle exact, but in practice approximations are necessary, and for large and complex systems KSDFT provides a higher accuracy for a given cost. The road to improving its accuracy involves research to design more accurate density functionals.

KSDFT is an example of a self-consistent-field (SCF) method, analogous to the Hartree-Fock method, which is an SCF method in WFT. In an SCF method, each electronic orbital is governed by an effective potential energy function (mentioned above), which is called the field.

For example, in Hartree-Fock theory the field is the average electrostatic field due to the nuclei and to the electronic charge distribution corresponding to the orbitals occupied by the other electrons; this field includes both direct Coulomb interactions and the effect of quantum mechanical exchange of identical electrons. In KSDFT the field is determined from a functional of the density. In either SCF method, the first step is that the orbitals are determined from an approximate field, then more accurate fields are calculated from the resulting orbitals, and new orbitals are found in these new fields; the process is iterated to self-consistency. The Kohn-Sham SCF method is more accurate than the Hartree-Fock one because the latter does not account for dynamical correlation of the electrons, that is, the tendency for two electrons to correlate their motion to minimize their mutual repulsion. In WFT, dynamical correlation is usually determined by post-Hartree-Fock methods that correlate the electrons in non-self-consistent approximations; even though these post-Hartree-Fock steps are not self-consistent, they are very expensive, especially for large and complex systems. In contrast, KSDFT includes dynamical correlation during the SCF step by writing the density functional as the sum of an exchange functional and a correlation functional, where the latter includes dynamical correlation. The field calculated from this density functional incorporates the energetic effect of electron correlation in an approximate way. (It is approximate because we do not know the exact exchange-correlation potential for real systems.) The exchange functional includes electron exchange, which lowers the energy of the electronic subsystem by allowing electrons, which are indistinguishable, to exchange spin orbitals with one another. In contrast, exchange is included exactly in Hartree-Fock theory by obtaining a variationally correct energy for an antisymetrized wave function; this leads to a nonlocal field in Hartree-Fock theory, that is, the field depends not just on local values of the orbitals or density and their local derivatives, but on an integration over all space.

The approximate density functionals in the literature may be classified as local and nonlocal. For local functionals, the exchange-correlation part of the self-consistent field at a given point in space depends on the spin densities and possibly on their derivatives and on the spin-up and spin-down kinetic energy densities at that point in space (some functionals, although none of them discussed in this review, substitute the Laplacian of the spin density for the spin kinetic energy density); for nonlocal functionals, the exchange-correlation part of the self-consistent field at a given point in space involves a nonlocal integral over all space. The only widely studied (to date) method to include nonlocality is to incorporate Hartree-Fock exchange; functionals involving Hartree-Fock exchange are called hybrid. Recently some groups developed nonlocal correlation functionals based on the random-phase approximation (Furche 2008; Scuseria et al. 2008). In order of increasing complexity and accuracy, the three types of local functionals are the local spin density approximation (LSDA) (Kohn and Sham 1965), generalized gradient approximation (GGA) (Langreth and Mehl 1983; Becke 1988; Lee et al. 1988; Perdew et al. 1992, 1996; Zhao and Truhlar 2008b), and meta-GGAs (Becke 1996; Tao et al. 2003; Grüning et al. 2004; Zhao and Truhlar 2006b, 2008c). Nonlocal functionals include hybrid GGAs and hybrid meta functionals. Hybrid GGAs and hybrid meta functionals (both of which include nonlocal Hartree-Fock exchange) have better performance for general-purpose applications in chemistry than local functionals, but tend to be less accurate, all other considerations being equal, for systems with nearly degenerate configurations, such as a transition metal atom with nearly degenerate $s^2 d^{n-1}$ and sd^{n-1} configurations. Systems with nearly degenerate configurations are usually called multireference systems (Truhlar 2007).

Note that meta and hybrid terms in a density functional depend on occupied orbitals, not just on the density and its derivatives; the exchange-correlation energy is nevertheless still a functional of the density because formally the orbitals are functionals of the density. The most complete density functionals (such as the random phase ones mentioned above) also include terms that depend on unoccupied orbitals; such functionals are not discussed in detail in the present review.

One hybrid GGA, namely B3LYP (Becke 1988, 1993; Lee et al. 1988; Stephens et al. 1994), has become extraordinary popular (Sousa et al. 2007) in theoretical and computational chemistry. However, B3LYP and other popular functionals have unsatisfactory performance issues such as: 1) underestimation of barrier heights (Zhao et al. 2005a); 2) underestimation of interaction energies for weak noncovalent interactions (Zhao and Truhlar 2008e); and 3) underestimation of bond energies in transition metal compounds (Reiher et al. 2001; Schultz et al. 2005a,b; Harvey 2006). Some recent studies have shown that these shortcomings lead to large systematic errors in the prediction of heats of formation of organic molecules (Woodcock et al. 2002; Check and Gilbert 2005; Izgorodina et al. 2005; Grimme 2006; Schreiner et al. 2006; Wodrich et al. 2006; Zhao and Truhlar 2006a; Wodrich et al. 2007) and incorrect trends in the bond energies of organometallic catalytic systems (Tsipis et al. 2005; Zhao and Truhlar 2007b).

Since 2001, the Minnesota theoretical chemistry group has done extensive work in designing and optimizing more accurate density functionals, and these efforts resulted in several new functionals; eight of those developed in the 2005-2008 time frame are called the Minnesota density functionals (with acronyms beginning with M05, M06, or M08), and the full set of functionals developed at the University of Minnesota may be called University of Minnesota density functionals. In the next section, we review the functionals developed at the University of Minnesota, including some of their validations, and in the rest of the article, we review selected recent applications of University of Minnesota functionals in problems related to mineralogy and geochemistry. For applications of other density functionals and/ or applications in other areas, we recommend some recent reviews (Scuseria and Staroverov 2005; Cramer and Truhlar 2009) as well as a nontechnical introduction to five of the first six Minnesota functionals (Zhao and Truhlar 2008c).

UNIVERSITY OF MINNESOTA FUNCTIONALS

Table 1 lists, in chronological order, the functionals that have been developed by the Minnesota theoretical chemistry group. Although the doubly hybrid functionals (Zhao et al. 2004b) and multicoefficient density functional methods (Zhao et al. 2005b) developed by us can be viewed as generalized density functionals, we did not include them in Table 1 because the energy functional includes unoccupied orbitals, and we have restricted our scope to not discuss such work in detail in the present review.

MPW1K (Lynch et al. 2000) and BB1K (Zhao et al. 2004a) were optimized against a database of barrier heights by using the adiabatic connection method, and both of them were designed for kinetics. In 2004, we also developed MPWB1K and MPW1B95 (Zhao and Truhlar 2004); MPWB1K was designed for kinetics, but it has been shown to have improved performance for noncovalent interactions, and MPW1B95 was designed for main-group thermochemisty. TPSS1KCIS is a byproduct of our work in multicoefficient density functional methods (Zhao et al. 2005b). MPW1KCIS and MPWKCIS1K are byproducts of our nonhydrogen transfer barrier height database work (Zhao et al. 2005a), whereas PBE1KCIS is a byproduct of our noncovalent database work (Zhao and Truhlar 2005a). In 2005, Dahlke and Truhlar (2005) developed three functionals for describing energetics in water clusters, namely PBE1W, PBELYP1W, and TPSSLYP1W.

Also in 2005, PWB6K and PW6B95 (Zhao and Truhlar 2005b) were developed by reoptimizing six parameters in the MPWB1K functional form; PWB6K was shown to have greatly improved performance for noncovalent interactions (Zhao and Truhlar 2005c,d; Zhao et al. 2005d). However, from two benchmark studies in transition metal chemistry (Schultz et al. 2005a,b), we found a dilemma for the performance of density functionals, that is, to obtain more accurate barrier heights, one needed to mix in a high percentage of Hartree-

Table 1. Minnesota functionals.

Functional	Type[a]	Year	Reference
MPW1K	HG	2000	(Lynch et al. 2000)
BB1K	HM	2004	(Zhao et al. 2004a)
MPWB1K	HM	2004	(Zhao and Truhlar 2004)
MPW1B95	HM	2004	(Zhao and Truhlar 2004)
MPW3LYP	HG	2005	(Zhao and Truhlar 2004)
TPSS1KCIS	HM	2005	(Zhao et al. 2005b)
MPW1KCIS	HM	2005	(Zhao et al. 2005a)
MPWKCIS1K	HM	2005	(Zhao et al. 2005a)
PBE1KCIS	HM	2005	(Zhao and Truhlar 2005b)
PW6B95	HM	2005	(Zhao and Truhlar 2005b)
PWB6K	HM	2005	(Zhao and Truhlar 2005b)
MPWLYP1M	HG	2005	(Schultz et al. 2005b)
MOHLYP	G	2005	(Schultz et al. 2005b)
MPWLYP1W	G	2005	(Dahlke and Truhlar 2005)
PBE1W	G	2005	(Dahlke and Truhlar 2005)
PBELYP1W	G	2005	(Dahlke and Truhlar 2005)
TPSSLYP1W	M	2005	(Dahlke and Truhlar 2005)
M05	HM	2005	(Zhao et al. 2005c)
M05-2X	HM	2006	(Zhao et al. 2006)
M06-L	HM	2006	(Zhao and Truhlar 2006b)
M06-HF	HM	2006	(Zhao and Truhlar 2006g)
M06	HM	2008	(Zhao and Truhlar 2008e)
M06-2X	HM	2008	(Zhao and Truhlar 2008e)
SOGGA	G	2008	(Zhao and Truhlar 2008b)
M08-HX	HM	2008	(Zhao and Truhlar 2008d)
M08-SO	HM	2008	(Zhao and Truhlar 2008d)

[a]G: GGA; M: meta-GGA; HG: hybrid GGA; HM: hybrid meta GGA

Fock exchange, whereas transition metal chemistry favors low percentages of Hartree-Fock exchange; MOHLYP and MPWLYP1M are two byproducts of these benchmark studies.

In order to develop a functional that can handle barrier heights, noncovalent interactions, and transition metal chemistry, we developed the M05 functional (Zhao et al. 2005c, 2006) and it has good performance for transition metal chemistry (Zhao and Truhlar 2006e) as well as main-group thermochemistry, barrier heights, and noncovalent interactions. With the same functional form as M05, we developed the M05-2X functional (Zhao et al. 2006) that focuses on main-group chemistry, barrier heights, and noncovalent interactions (Zhao and Truhlar 2006a,c,d,f, 2007b,c).

In 2006, building on all this experience, we have developed four new functionals by combining the functional forms of the M05 (Zhao et al. 2005c, 2006) and VSXC (Voorhis and Scuseria 1998) functionals; they are called the M06-class functionals: (a) M06, a hybrid meta functional, is a functional with good accuracy "across-the-board" for transition metals, main group thermochemistry, medium-range correlation energy, and barrier heights. (b) M06-2X, another hybrid meta functional, is not good for transition metals but has excellent performance for main group chemistry, predicts accurate valence and Rydberg electronic excitation energies, and is an excellent functional for chemical reaction barrier heights and aromatic-aromatic

stacking interactions. (c) M06-L is not as accurate as M06 or M06-2X for barrier heights but is the most accurate functional for the energetics of systems containing transition metals and is the only local functional (no Hartree-Fock exchange) with better across-the-board average performance than B3LYP; this is very important because only local functionals are affordable for many demanding applications on very large systems. (d) M06-HF has good performance for valence, Rydberg, and charge transfer excited states with minimal sacrifice of ground-state accuracy. In a recent review (Zhao and Truhlar 2008c), we compared the performance of the M06-class functionals and one M05-class functional to that of some popular functionals for diverse databases and for some difficult cases. For most purposes, the M05 and M06-2X functionals may be considered to simply be earlier versions of the M06 and M06-2X functionals.

In 2008, we explored the limit of accuracy attainable by a global hybrid meta density functional for main-group thermochemistry, kinetics, and noncovalent interactions by using a very flexible functional form called M08 (Zhao and Truhlar 2008d). M08-HX and M08-SO were developed in that exploratory study; they improve on M06-2X, but only a little (Zhao and Truhlar 2008d), and they have excellent performance for barrier heights (Zheng et al. 2009).

In 2008, we also developed a nonempirical GGA, which is exact through second order in a gradient expansion, that is, in terms of an expansion in powers of the gradient of the density, and it is called the second-order generalized gradient approximation (SOGGA). The SOGGA functional differs from other GGAs in that it enforces a tighter Lieb-Oxford bound on the density functional (Zhao and Truhlar 2008b). SOGGA and other functionals have been compared to a diverse set of lattice constants, bond distances, and energetic quantities for solids and molecules.

In chemistry, the quality of a density functional is usually judged on the basis of its predictions for energetic quantities such as thermochemistry and chemical reaction barrier heights, with less emphasis on geometric predictions, which are in some sense easier to predict at least qualitatively correctly. In solid-state chemistry and physics, though, there is often a great emphasis on predicting precise geometrical parameters, such as lattice constants of solids. In many cases, good geometric predictions for molecules (bond lengths, bond angles, etc.) are correlated with good predictions for lattice constants. One somewhat exceptional case is M06-L, which has exceptionally good performance for predicting molecular geometries (Zhao and Truhlar 2008d), but only so-so quality for predicting lattice constants (Zhao and Truhlar 2008b); however the SOGGA functional, which is not as good as M06-L for broad applications, has excellent performance for lattice constants (Zhao and Truhlar 2008b).

In the next section, we review some recent validations and applications of the Minnesota functionals for problems related to mineralogy and geochemistry. We recommend consulting the original references in Table 1 for the general performance of the Minnesota functionals in other areas of chemistry.

The orbital solutions of the SCF equations are usually determined variationally as linear combinations of basis functions. For molecular calculations, the basis functions are usually Gaussians. For calculations on condensed-phase systems (solids, liquids, gas-solid surfaces), the orbitals are sometimes expanded in plane waves. In an ideal world the basis sets would be complete, but in practice they are often truncated, which can contribute some error if the truncation is too severe. Standard truncated sets of Gaussian functions are available, and some examples mentioned in this review are (in order of increasing completeness) 6-31G(d,p), 6-31+G(d,p), TZVP(P), 6-311++(2d,2p), 6-311+G(2df,2p), and aug-cc-pVTZ; we refer the reader to the original publications for further details of these basis sets. When specifying a KSDFT calculation using Gaussian basis functions, a common convention (used in some places in this article) is to label the method as *F/B*, where *F* is the density functional, and *B* is the basis set.

VALIDATIONS AND APPLICATIONS

Water and aqueous chemistry

The chemistry of ground water is one of the most important subjects in geoscience. It is important to benchmark the quality of density functionals for the description of interactions between water molecules, and one of the most definitive ways to do this is to validate them against accurate WFT calculations for small water clusters for which accurate WFT calculations are possible. In 2008, Dahlke et al. (2008b) assessed the performance of 7 density functionals for reaction energies in hydronium, hydroxide, and pure water clusters, and they found that the M06-L functional is very promising for condensed-phase simulations of the transport of hydronium and hydroxide ions in aqueous solution. In another paper, Dahlke et al. (2008a) assessed the accuracy of 11 density functionals for prediction of relative energies and geometries of low-lying isomers of water hexamers, and their calculations show that only three density functionals, M06-L, M05-2X, and M06-2X, are able to correctly predict the relative energy ordering of the hexamers when single-point energy calculations are carried out on geometries obtained with second-order Møller-Plesset perturbation theory (MP2). Of the tested 11 density functionals, the most accurate density functionals for relative energies in water hexamer are PWB6K, MPWB1K, and M05-2X.

More recently, Bryantsev et al. (2009) evaluated the accuracy of the B3LYP, X3LYP, M06-L, M06-2X, and M06 functionals to predict the binding energies of neutral and charged water clusters. They ranked the accuracy of the functionals on the basis of the mean unsigned error (MUE) between calculated benchmark and density functional theory energies, and they found that M06-L (MUE = 0.73 kcal/mol) and M06 (MUE = 0.84) give the most accurate binding energies using very extended basis sets such as aug-cc-pV5Z. For more affordable basis sets, the best methods for predicting the binding energies of water clusters are M06-L/aug-cc-pVTZ (MUE = 1.24 kcal/mol), B3LYP/6-311++G(2d,2p) (MUE = 1.29 kcal/mol), and M06/aug-cc-pVTZ (MUE = 1.33 kcal/mol).

Austin et al. (2009) recently benchmarked several functionals for actinyl complexes and found that the M06 functional is competitive with high-level CCSD(T) methods in the study of the water exchange mechanism of the $[UO_2(OH_2)_5]^{2+}$ ion and of the redox potential of the aqua complexes of $[AnO_2]^{2+}$ (An = U, Np, and Pu).

In order to learn about reactions between oxide minerals and aqueous solutions, Qian et al. (2009) employed the MPWKCIS1K and B3LYP functionals to study the water exchange mechanism of the polyoxocation $GaO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ in aqueous solution. They found that the reactant, modeled as the polyoxocation already specified plus 15 second-solvation-shell water molecules plus a continuum solvent model for the rest of the aqueous solvent, first loses a water ligand to form an intermediate with a five-coordinated aluminum atom. After that, the incoming water molecule in the second coordination shell attacks the intermediate with a five-coordinated aluminum atom to produce the product. The calculations imply, as should be expected, that both the explicit water molecules in the second hydration sphere and the bulk solvent water have a significant effect on the energy barriers; the need to carry out calculations on a large model is one of the reasons why the relatively inexpensive KSDFT is a preferred method for this kind of calculation.

Tommaso and Leeuw (2009) recently employed the MPW1B95 functional to study the dimerization of calcium carbonate in aqueous solution under natural water conditions. Their calculations suggest that, at $T = 298$ K and neutral pH conditions, the oligomerization of calcium carbonate is not spontaneous in water. This is an indication that the nucleation of calcium carbonate may not occur through a homogeneous process when calcium-bicarbonate ion pairs are the major source of $CaCO_3$ in the aqueous environment.

Goumans et al. (2009b) employed MPWB1K to study the formation of water on a model dust grain (fosterite) by using an embedded cluster approach. They found that the formation of water on a bare dust grain from hydrogen and oxygen atoms is catalyzed by an olivine surface by stabilizing the reaction intermediates and product.

Many studies of aqueous reactions are not directly relevant to geochemistry but show how complex processes in aqueous solution are becoming more amenable to study. For example, Wu et al. employed BB1K to study the mechanism of aqueous-phase asymmetric transfer hydrogenation of a ketone, in particular acetophenone, with HCOONa catalyzed by ruthenium *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine (Wu et al. 2008). The reaction has a nonconcerted hydrogen transfer as the rate-limiting step in water, as compared to a rate-limiting step of concerted proton transfer and hydride formation/transfer in isopropanol solvent. The calculations revealed that in aqueous solution water hydrogen bonds to the ketone oxygen at the transition state for hydrogen transfer, lowering the energy barrier by about 4 kcal/mol.

Oxidation-reduction (redox) processes (Winget et al. 2000, 2004; Patterson et al. 2001; Belzile et al. 2004; Lewis et al. 2004, 2007; Anbar et al. 2005; Southam and Saunders 2005; MacQuarrie and Mayer 2005; Charlet et al. 2007; Savage et al. 2008; Helz et al. 2008) are very important in geochemistry. Oxidation and reduction of metal ions in aqueous solution are a particularly important example. Jaque et al. (2007) calculated the standard reduction potential of the $Ru3^+|Ru^{2+}$ couple in aqueous solution with 37 density functionals, including BB1K, MPW1B95, MPW1KCIS, MPWKCIS1K, PBE1KCIS, MPWB1K, and TPSS1KCIS, and five basis sets. Either one solvent shell (six water molecules) or two solvent shells (18 water molecules) were treated explicitly, and the rest of the solvent was treated as a dielectric continuum. The calculated difference in solvation free energies of Ru^{3+} and Ru^{2+} varies from -10.56 to -10.99 eV for six waters and from -6.83 to -7.45 eV for 18. The aqueous standard reduction potential is overestimated when only the first solvation shell is treated explicitly, and it is underestimated when the first and second solvation shells are treated explicitly. This study shows the danger of simply choosing a single methodology without examining the dependence of the results on the choice of functional and model.

Atmospheric chemistry

Another important subject in geochemistry is atmospheric chemistry, and the Minnesota functionals have also been applied in this area (Lin et al. 2005; Eillngson et al. 2007; Ellingson and Truhlar 2007).

Isotopic analysis is an important technique for understanding the production, transport, and depletion of various species in the atmosphere (McCarthy et al. 2001, 2003; Keppler et al. 2005), and the fractionation of ^{12}C and ^{13}C in reactions of methane with OH and Cl are important parameters in this analysis. We (Lin et al. 2005; Ellingson et al. 2007) calculated the kinetic isotope effect and its temperature dependence for the reactions of $^{12}CH_4$ and $^{13}CH_4$ with OH using the BB1K, MPW1K, and M06-2X density functionals as well as three high-level multicoefficient methods, including two based in part on density functionals using unoccupied orbitals. Later experimental work led to the conclusion that the tunneling effect is underestimated in these calculations (Sellevåg et al. 2006).

The reaction of OH with H_2S plays an important role in regulating the amount of H_2S in the atmosphere, and therefore its reaction rate is an important input in atmospheric modeling (Perry et al. 1976). This reaction apparently has an unusual temperature dependence, with a negative or very small temperature dependence in at least part of the range of atmospheric temperatures (~200-300 K) and a positive temperature dependence at higher temperatures. A negative temperature dependence is often indicative of a reaction for which the dynamical bottleneck lies in a region where the potential energy of interaction of the reactants is attractive. Thus, in order to model the temperature dependence of this reaction reliably over the whole

range, one requires a density functional that is accurate for both reaction barriers and attractive forces. Calculations based on the M06-2X density functional, which is notable for being more accurate than previous density functionals for both of these features, reproduced the unusual temperature dependence found experimentally, whereas calculations based on older density functionals did not (Ellingson and Truhlar 2007).

Recently, Vega-Rodriguez and Alvarez-Idaboy (2009) employed the MPWB1K and M05-2X density functionals to study the mechanism for the reactions of OH with unsaturated aldehydes, which are of importance for atmospheric chemistry. They found that the calculated rate constants with M05-2X are in good agreement with experiments.

Metal oxides

Most metals found in the Earth's crust exist as silicate, oxide, and/or sulfide minerals. Metal oxide materials are particularly interesting for their technological usefulness in areas such as catalysis, photovoltaics, and electronics.

Recently, Sorkin et al. (2008) reported a systematic study of small iron compounds including FeO^-. They found that some of the improvements that were afforded by the semiempirical +U correction (widely employed in condensed-matter physics) could also be accomplished by improving the quality of the exchange-correlation functional.

Benchmark databases for Zn-containing molecules (including ZnO, Zn_2O_2, Zn_3O_3, and Zn_4O_4) have been recently developed by Amin and Truhlar (2008) and Sorkin et al. (2008), including Zn-ligand bond distances, angles, dipole moments, and bond dissociation energies. They tested many density functionals against these benchmark databases, and they found that the best KSDFT method to reproduce dipole moments and dissociation energies of the benchmark Zn compound database is M05-2X.

M05-2X has been employed to investigate the mechanism of the photocatalytic degradation of 1,5-naphthalenedisulfonate (a surfactant) on colloidal TiO_2 (Szabo-Bardos et al. 2008). The degradation is initiated by oxidative attack of an OH radical to make an aromatic-OH adduct. M05-2X calculations allowed a comparative analysis of possible sites of attack by the radical.

The adsorption of CO on the (001) surface of MgO is a challenge for popular density functionals because of its weak interaction character. Valero et al. show that M06-2X and M06-HF are the first two functionals to provide a simultaneously satisfactory description of adsorbate geometry, vibrational frequency shift, and adsorption energy of CO on the (001) surface of MgO (Valero et al. 2008).

Silicates and siliceous minerals

Silicate minerals and silica make up the largest part of the crust of the Earth. The structure, protonation, and reactivity of silicates and compounds containing silicon-oxygen bonds have been widely studied by quantum mechanics (Shambayati et al. 1990; Blake and Jorgensen 1991; Tossell and Sahai 2000; Avramov et al. 2005; Vuilleumier et al. 2009). Zhang et al. (2007) investigated the computational requirements for simulating the structures and proton activity of silicaceous materials. In their study, 14 density functionals in combination with 8 basis sets were tested against high-level wave-function-based methods. They found that the most accurate density functional for both geometries and energetics is M05-2X.

Zwijnenburg et al. (2008) compared the performance of B3LYP and BB1K for the prediction of optical excitations of defects in nanoscale silica clusters. They found that the spatially localized excitations are well described by time-dependent KSDFT, but B3LYP gives excitation energies that are significantly underestimated in the case of the charge-transfer excitations. In contrast, the time-dependent KSDFT calculations with BB1K was found to give generally good excitation energies for the lowest excited states of both localized and charge-transfer excitations.

Goumans et al. (2008) employed MPWB1K to investigate the catalytic effect of a negatively charged silica surface site on addition reactions to an adsorbed unsaturated organic molecule using an embedded cluster approach. Their calculations show that a negatively charged defect on a silica surface (silanolate) effectively catalyzes the addition of H or O atom to the HCCH, $H_2C=CH_2$, or CO molecule adsorbed on it. The negative charge polarizes and destabilizes the multiple bonds, which in turn lowers the barriers to addition. These results indicate that complex interstellar molecules could be formed effectively via surface-catalyzed hydrogenation and/or oxidation routes.

The mineral olivine is a magnesium iron silicate with the formula $(Mg,Fe)_2SiO_4$, and it is one of the most common minerals on Earth. Recently MPWB1K has been employed to study the formation of H_2 on an olivine surface (Goumans et al. 2009a), and the results show that the forsterite surface catalyzes H_2 formation by providing chemisorption sites for H atoms. The calculations also indicate that pristine olivine surfaces should be good catalysts for H_2 formation, with low product excitation and high reaction efficiencies.

Morrow et al. (2009) used M05-2X to investigate the dissolution mechanism in aluminosilicate minerals. Their calculations show that Al species from protonated and neutral Al-O-Si sites can leach before Si species. Nangia and Garrison (2009) used the M05-2X density functional to study hydrolysis/precipitation reactions at silica surface sites. The barrier height data successfully explained the experimentally observed dissolution rate over the entire pH range.

Clay minerals such as montmorillonite are of interest as environmentally friendly catalysts supports and also possibly as catalysts on their own (Zhu et al. 2009; Briones-Jurado and Agacino-Valdés 2009).

Zeolites

Zeolites are microporous/nanoporous aluminosilicate minerals, and the zeolitic pores are nanocavities. Zeolites have the capability to catalyze chemical reactions that take place in their internal cages, and they provide a size-selective environment for chemical reactions. Theorefore zeolites are widely used in industry as heterogenenous catalysts. Indeed "every drop of gasoline we burn in our car has seen at least one zeolite catalyst on its way through the refinery" (Sauer 2006). Although industrial zeolites needed for specialized applications are synthesized to obtain the required purity and uniformity and sometimes to obtain unnatural frameworks, many naturally occuring zeolites are known, and zeolite-rich formations have both diagenetic and volcanic origins.

Practical applications of quantum mechanical calculations to reactions in extended systems like zeolites can be carried out by using the ONIOM method or the QM/MM method. In ONIOM calculations (Morokuma 2002), one treats a reaction site (subsystem) by a quantum mechanical method, and the rest of the system (the surrounding atoms and molecules) by a less expensive quantum mechanical method or an analytic potential energy function; when one treats the surroundings by molecular mechanics (that is, an analytical potential energy function—such as the UFF force field (Rappé et al. 1992)—that is parameterized for nonreactive systems or nonreactive subsystems (Hagler and Ewig 1994; Cygan 2001)), this is usually called a combined quantum mechanical and molecular mechanical (QM/MM) calculation (Lin and Truhlar 2007). An ONIOM or QM/MM calculation is usually denoted $A:B$, where A denotes the more expensive method used for the reactive subsystem, and B denotes the less expensive method used for the surroundings. In QM/MM calculations, A denotes the QM part, and B denotes the MM part.

BB1K was employed by To et al. (2006b) to investigate the mechanism of the formation of heteroatom active sites in zeolites, and the calculations show that the tetravalent-heteroatom sites preferentially adopt tripodal configurations, whereas the hydrolysis of T-O-Si bridges (T

is a heteroatom such as Ti or Sn) helps to relieve lattice strain and to stabilize the structure. Thus hydrolysis and inversion play important roles in the stabilization of heteroatom-based active sites in zeolites. In a subsequent paper, To et al. (2006a) reported QM/MM computations with BB1K for the QM active site in Ti-substituted zeolites (titanium silicalite-1) to study the processes of hydrolysis of Ti-O-Si linkages and inversion of the TiO_4 tetrahedra. The calculated structural features of the tetra- and tripodal Ti moieties are in good agreement with experiments, and suggest that the tripodal species dominate in hydrous conditions, and that this is likely to be the chemically active form. Later, To et al. (2007) employed the BB1K functional to study the interaction of water molecules with Ti sites in titanium silicalite-1, and they found that the hydrations of all Ti centers are exothermic, a result that is in good agreement with experiment and previous theoretical work. In 2008, they (To et al. 2008) employed BB1K to find the active oxidizing species in the H_2O_2/titanium silicalite-1 catalytic system, and their computational results indicate that water is not just a medium for transporting reactants and products; rather it has an active role in stabilizing the peroxo species present on the catalyst.

In 2008, we developed a benchmark database for interactions in zeolite model complexes based on CCSD(T) calculations, and we tested 41 density functionals against the new database (Zhao and Truhlar 2008a). Among the tested density functional methods, M06-L/6-31+G(d,p) gives a mean unsigned error (MUE) without counterpoise correction of 0.87 kcal/mol. With counterpoise corrections, the M06-2X (Zhao and Truhlar 2008e) and M05-2X (Zhao et al. 2006) functionals give the best performance. We also tested 10 functionals against the binding energies of four complexes (two noncovalent and two covalent) of the adsorption of isobutene on a large 16T zeolite model cluster (Fig. 1). The counterpoise corrected binding energies are shown in Table 2. For comparison Table 2 also shows WFT results obtained by treating dynamical correlation by second order perturbation theory; those results are labeled MP2.

Table 2 shows that M05-2X and M06-2X are the best performers for the binding energies in a model 16T zeolite cluster, followed by M06-L and M06, and these four functionals give a smaller MUE than the MP2/TZVP(P) method. The popular B3LYP functional performs poorly with an MUE of 16.6 kcal/mol. These results show that M06-L, M06, M05-2X, and M06-2X are very promising quantum mechanical methods for the QM part of QM/MM simulations of zeolite. This conclusion has been confirmed recently by Maihom et al. (2009). They investigated the mechanisms of ethene methylation with methanol and dimethyl ether in a 128T cluster of ZSM-5 zeolite using the ONIOM(B3LYP/6-31G(d,p):UFF) and ONIOM(M06-2X/6-311+G(2df,2p):UFF) methods with the zeolitic Madelung potential generated by the surface charge representation of the electrostatic embedding potential (SCREEP) method (Vollmer et al. 1999). Their calculations show that the energies for the adsorption of methanol and dimethyl ether on H-ZSM-5 from an ONIOM2(M06-2X/6-311+G(2df,2p):UFF)+SCREEP calculation are in good agreement with the experimental data.

Boekfa et al. (2009) employed four ONIOM methods, namely (MP2:M06-2X), (MP2:B3LYP), (MP2:HF), and (MP2:UFF), to investigate the confinement effect on the adsorption and reaction mechanism of unsaturated aliphatic, aromatic and heterocyclic compounds on H-ZSM-5 zeolite. They found that (MP2:M06-2X) give the best agreement with experiments for the energies of adsorption of ethene, benzene, ethylbenzene, and pyridine on H-ZSM-5.

Kumsapaya et al. (2009) employed the M06-L/6-31G(d,p):UFF ONIOM method to investigate the isomerization of 1,5- to 2,6-dimethylnaphthalene over acidic β zeolite. The results in their study show the excellent performance of a combination of the M06-L functional with the confinement effect represented by the universal force field for investigating the transformations of aromatic species zeolite systems.

Hydroxyl nests are formed in zeolites, especially the all-silicon silacalite-1 (Astorino et al. 1995; Kalipcilar and Culfaz 2000), at a defect involving a missing silicon or aluminum
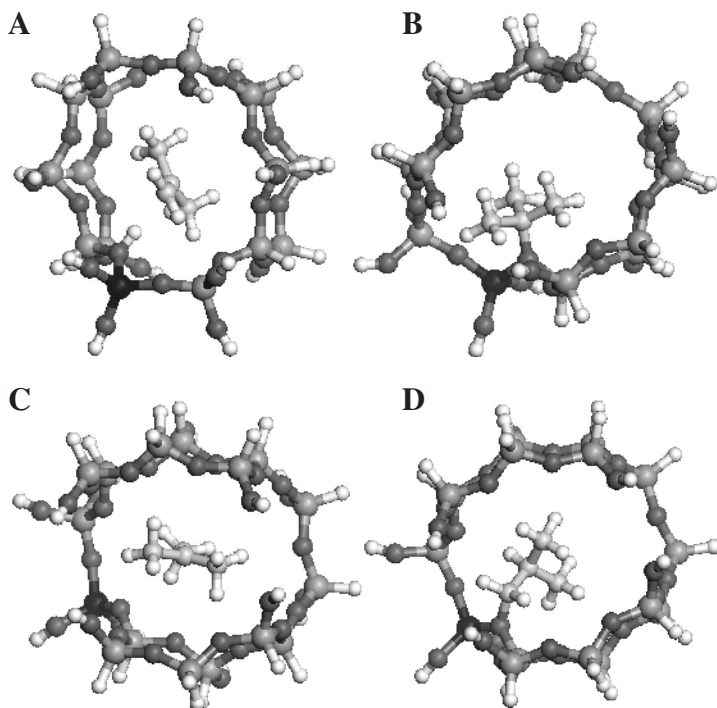
Figure 1. Geometries of the 16T zeolite model complexes. (A) 16T·isobutene π complex, (B) 16T *tert*-butoxide, (C) 16T *tert*-butyl carbenium ion, (D) 16T isobutoxide.

atom; the nest consists of four hydrogen-bonded hydroxyl groups. BB1K has been recently employed to study high-temperature dehydrogenation of defective silicalites (Fickel et al. 2010). The combined experimental and computational study indicates that the product of the dehydroxylation of hydroxyl nests in silicalite-1 is not water but hydrogen.

To et al. (2005) employed BB1K to investigate the ground state and the electronically excited states of the $[AlO_4]^0$ hole in α-quartz and in the siliceous zeolite ZSM-5. Their results show that BB1K is significantly more accurate and reliable than previous popular density functionals, and the BB1K excitation energies show excellent agreement with experiment.

Mineral nanoparticles

Many mineral accumulations are only poorly crystalline or exist as nanoparticles with properties quite different than those of microcrystals or macroscrtystals; transmission electron microscopy can be used to probe their nanomorphology (Penn et al. 2001; Hochella et al. 2008; Isaacson et al. 2009). Computational methods based on electronic structure theory are well suited for studying the structure, dynamics, and phase properties of small particles, such as metal and metal oxide clusters and nanoparticles, as shown for example in recent work on aluminum nanoparticles (Li et al. 2007; Li and Truhlar 2008a,b).

In recent work, the SOGGA, M06, and M06-L density functionals have been found to be uniquely successful for predicting the structures of small anionic gold clusters (Mantina et al. 2009), and in other recent work M06-L was found to be uniquely successful in predicting the structures of small cationic gold clusters (Ferrighi et al. 2009) (M06 and SOGGA were not included in the latter study).

Table 2. Binding energies (kcal/mol) in four complexes involving the adsorption of isobutene on a 16T zeolite cluster model.[a]

Method[b]	π complex	tert-butoxide	tert-butyl carbenium ion	isotutoxide	MUE[c]
Best estimate[d]	15.1	13.9	−9.8	13.9	
M05-2X	11.7	14.9	−8.1	14.0	1.6
M06-2X	12.7	16.6	−9.1	15.6	1.9
M06-L	14.4	15.6	−2.3	13.5	2.6
M06	13.3	16.0	−3.9	14.4	2.6
M06-HF	12.4	18.6	−12.5	18.8	3.7
MP2/TZVP(P)	10.8	10.0	−13.4	9.1	4.1
PBE0	2.9	4.7	−15.6	4.7	9.1
PBE	3.2	2.3	−12.8	2.0	9.6
B97-1	3.9	2.2	−14.3	2.9	9.6
TPSSh	−0.9	1.8	−17.7	1.6	12.1
B3LYP	−2.5	−5.5	−20.7	−4.8	16.6

[a]See Figure 1 for the 16T model cluster and four complexes. All results are taken from a previous paper (Zhao and Truhlar 2008a).

[b]The 6-311+G(2df,2p) basis set is employed for all density functionals in this table; the basis set for the MP2 calculations in indicated after /.

[c]MUE denotes mean unsigned error (same as mean absolute deviation, MAD).

[d]Best estimates were calculated from the two last rows in Table 3 of Tuma and Sauer (2006). The geometries, and MP2/TZVP(P) results are also from Tuma and Sauer (2006). Other results in this table are from the present work.

CONCLUDING REMARKS

In this chapter, we have presented an introduction to the Minnesota density functionals. We reviewed some encouraging validations and applications of the Minnesota functionals in problems important for mineralogy and geochemistry. Since the new-generation Minnesota functionals have been designed to give broad accuracy in chemistry, they perform very well even for many difficult cases where popular functionals fail badly (Zhao and Truhlar 2008c). The prospects for successful further application to a number of problems in mineralogy and geochemistry are encouraging.

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