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14. ABSTRACT
We developed two new orbital-dependent density functionals, M08-HX and M08-SO that have excellent performance for predicting noncovalent interactions and chemical reaction barrier heights. We carried out several applications, tests, and validations of density functional theory to problems relevant to catalysis to learn and document the capabilities of density functional theory for this kind of work and to expose possible areas where improvement is needed. Our test systems included the Grubbs metathesis catalysts, Pd coordination compounds, and graphene, all three of which are subjects of recent Nobel Prizes, and we found encouragingly good performance of the Minnesota functionals in each case. We also had dramatic success for gold clusters. We created a catalytic energies database and used it to test 34 density functionals, finding the best performance for the Minnesota functionals. We also studied NMR chemical shielding constants, semiconductor band gaps, reactions of ozone, charge polarization effects, basis sets, reaction energies, actinoid chemistry, and geochemistry.

15. SUBJECT TERMS
density functional theory; catalysis; quantum chemistry; chemical reactions; computational chemistry

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832. "Improved Description of Nuclear Magnetic Resonance Chemical Shielding Constants Using the M06-L Meta-Generalized Gradient Density Functional," Y. Zhao and D. G. Truhlar, Journal of Physical Chemistry A **112**, 6794-6799 (2008). dx.doi.org/10.1021/jp804583d

> The performance of the M06-L density functional has been tested for four databases of NMR isotropic chemical shielding constants. Comparison with the B3LYP, BLYP, HCTH, KT1, KT2, LSDA, OPBE, OLYP, PBE, TPSS, and VSXC functionals shows that M06-L has improved performance for calculating NMR chemical shielding constants, especially for highly correlated systems. We also found that VSXC and M06-L have encouraging accuracy for calculating ^{13}C chemical shielding constants, and both functionals perform very well for the chemical shielding constants in the *o*-benzyne molecule.

836. "Exploring the Limit of Accuracy of the Global Hybrid Density Functional for Main-Group Thermochemistry, Kinetics, and Noncovalent Interactions," Y. Zhao and D. G. Truhlar, Journal of Chemical Theory and Computation **4**, 1849-1868 (2008). dx.doi.org/10.1021/ct800246v

> The hybrid meta density functionals M05-2X and M06-2X have been shown to provide broad accuracy for main group chemistry. In this article we make the functional form more flexible and improve the self-interaction term in the correlation functional to improve its self-consistent-field convergence. We also explore the constraint of enforcing the exact forms of the exchange and correlation functionals through second order (SO) in the reduced density. The hybrid meta density functionals M05-2X and M06-2X have been shown to provide broad accuracy for main group chemistry. In the present article we make the functional form more flexible and improve the self-interaction term in the correlation functional to improve its self-consistent-field convergence. We also explore the constraint of enforcing the exact forms of the exchange and correlation functionals through second order (SO) in the reduced density gradient. This yields two new functionals called M08-HX and M08-SO, with different exact constraints. The new functionals are optimized against 267 diverse main-group energetic data consisting of atomization energies, ionization potentials, electron affinities, proton affinities, dissociation energies, isomerization energies, barrier heights, noncovalent complexation energies, and atomic energies. Then the M08-HX, M08-SO, M05-2X, and M06-2X functionals and the popular B3LYP functional are tested against 250 data that were not part of the original training data for any of the functionals, in particular 164 main-group energetic data in 7 databases, 39 bond lengths, 38 vibrational frequencies, and 9 multiplicity-changing electronic transition energies. These tests include a variety of new challenges for complex systems, including large-molecule atomization energies, organic isomerization energies, interaction energies in uracil trimers,

and bond distances in crowded molecules (in particular, cyclophanes). The M08-HX functional performs slightly better than M08-SO and M06-2X on average, significantly better than M05- 2X, and much better than B3LYP for a combination of main-group thermochemistry, kinetics, noncovalent interactions, and electronic spectroscopy. Even more important than the improvement in accuracy afforded by M08-HX is the confirmation that the optimization procedure works well for data outside the training set. Problems for which the accuracy is especially improved by the new M08-HX functional include large-molecule atomization energies, noncovalent interaction energies, conformational energies in aromatic peptides, barrier heights, multiplicity-changing excitation energies, and bond lengths in crowded molecules.

842. "Benchmark Energetic Data in a Model System for Grubbs II Metathesis Catalysis and Their Use for Assessment and Validation of Electronic Structure Methods," Y. Zhao and D. G. Truhlar, Journal of Chemical Theory and Computation **5**, 324-333 (2009). dx.doi.org/10.1021/ct800386d

We present benchmark relative energetics in the catalytic cycle of a model system for Grubbs second-generation olefin metathesis catalysts. The benchmark data were determined by a composite approach based on CCSD(T) calculations, and they were used as a training set to develop a new spin-component-scaled MP2 method optimized for catalysis, which is called SCSC-MP2. The SCSC-MP2 method has improved performance for modeling Grubbs II olefin metathesis catalysts as compared to canonical MP2 or SCS-MP2. We also employed the benchmark data to test 17 WFT methods and 39 density functionals. Among the tested density functionals, M06 is the best performing functional. M06/TZQS gives an MUE of only 1.06 kcal/ mol, and it is a much more affordable method than the SCSC-MP2 method or any other correlated WFT methods. The best performing meta-GGA is M06-L, and M06-L/DZQ gives an MUE of 1.77 kcal/mol. PBE0 is the best performing hybrid GGA, with an MUE of 3.01 kcal/mol; however, it does not perform well for the larger, real Grubbs II catalyst. B3LYP and many other functionals containing the LYP correlation functional perform poorly, and B3LYP underestimates the stability of stationary points for the *cis*-pathway of the model system by a large margin. From the assessments, we recommend the M06, M06-L, and MPW1B95 functionals for modeling Grubbs II olefin metathesis catalysts. The local M06-L method is especially efficient for calculations on large systems.

851. "Calculation of Semiconductor Band Gaps with the M06-L Density Functional," Y. Zhao and D. G. Truhlar, Journal of Chemical Physics **130** 074103/1-3 (2009). dx.doi.org/10.1063/1.3076922.

The performance of the M06-L density functional has been tested for band gaps in seven semiconductors plus diamond and MgO. Comparison with the LSDA, BLYP, PBE, TPSS, and HSE functionals shows that M06-L has improved performance for calculating band gaps as compared to other local functionals, but it is less accurate than the screened hybrid HSE functional for band gaps.

855. "Thermochemical Kinetics for Multireference Systems: Addition Reactions of Ozone," Y. Zhao, O. Tishchenko, J. R. Gour, W. Li, J. J. Lutz, P. Piecuch, and D. G. Truhlar, Journal of Physical Chemistry A **113**, 5786–5799 (2009). dx.doi.org/10.1021/jp811054n.

The 1,3-dipolar cycloadditions of ozone to ethyne and ethene provide extreme

examples of multireference singlet-state chemistry, and they are examined here to test the applicability of several approaches to thermochemical kinetics of systems with large static correlation. Four different multireference diagnostics are applied to measure the multireference characters of the reactants, products, and transition states; all diagnostics indicate significant multireference character in the reactant portion of the potential energy surfaces. We make a more complete estimation of the effect of quadruple excitations than was previously available, and we use this with CCSDT/CBS estimation of Wheeler et al. (Wheeler, S. E.; Ess, D. H.; Houk, K. N. *J. Phys. Chem. A* **2008**, *112*, 1798) to make new best estimates of the van der Waals association energy, the barrier height, and the reaction energy to form the cycloadduct for both reactions. Comparing with these best estimates, we present comprehensive mean unsigned errors for a variety of coupled cluster, multilevel, and density functional methods. Several computational aspects of multireference reactions are considered: (i) the applicability of multilevel theory, (ii) the convergence of coupled cluster theory for reaction barrier heights, (iii) the applicability of completely renormalized coupled cluster methods to multireference systems, (iv) the treatment by density functional theory, (v) the multireference perturbation theory for multireference reactions, and (vi) the relative accuracy of scaling-type multilevel methods as compared with additive ones. It is found that scaling-type multilevel methods do not perform better than the additive-type multilevel methods. Among the 48 tested density functionals, only M05 reproduces the best estimates within their uncertainty. Multireference perturbation theory based on the complete-active-space reference wave functions constructed using a small number of reaction-specific active orbitals gives accurate forward barrier heights; however, it significantly underestimates reaction energies.

863. "Planar-to-Three-Dimensional Structural Transition in Anionic Gold Clusters," M. Mantina, R. Valero, and D. G. Truhlar, Journal of Chemical Physics **131**, 064706/1-5 (2009).

As gold clusters increase in size, the preferred structure changes from planar to three-dimensional and, for anionic clusters, Au_n^-, the two-dimensional →three-dimensional transition is found experimentally to occur between $n = 11$ and $n = 12$. Most density functionals predict that planar structures are preferred up to higher n than is observed experimentally, an exception being the local spin density approximation. Here we test four relatively new functionals for this feature, in particular, M05, M06-L, M06, and SOGGA. We find that M06-L, M06, and SOGGA all predict the 2D→3D transition at the correct value of n. Since the M06-L and M06 functionals have previously been shown to be reasonably accurate for transition metal bond energies, main group atomization energies, barrier heights, and noncovalent interaction energies, and, since they are here shown to perform well for the *s-d* excitation energy and ionization potential of Au atoms and for the size of Au_n^- clusters at which the 2D→3D transition occurs, they are recommended for simulating processes catalyzed by gold clusters.

869. "Density Functional Theory for Transition Metals and Transition Metal Chemistry," C. J. Cramer and D. G. Truhlar, Physical Chemistry Chemical Physics **11**, 10757–10816 (2009). dx.doi.org/10.1039/b907148b.

We introduce density functional theory and review recent progress in its application to transition metal chemistry. Topics covered include local, meta,

hybrid, hybrid meta, and range-separated functionals, band theory, software, validation tests, and applications to spin states, magnetic exchange coupling, spectra, structure, reactivity, and catalysis, including molecules, clusters, nanoparticles, surfaces, and solids.

876. "Tests of the RPBE, revPBE, τHCTHhyb, ωB97X-D, and MOHLYP Density Functional Approximations and 29 Others Against Representative Databases for Diverse Bond Energies and Barrier Heights in Catalysis," K. Yang, J. Zheng, Y. Zhao, and D. G. Truhlar, Journal of Chemical Physics **132**, 164117/1-10 (2010). dx.doi.org/10.1063/1.3382342 or link.aip.org/link/?JCP/132/164117.

> Thirty four density functional approximations are tested against two diverse databases, one with 18 bond energies and one with 24 barriers. These two databases are chosen to include bond energies and barrier heights which are relevant to catalysis, and in particular the bond energy database includes metal-metal bonds, metal-ligand bonds, alkyl bond dissociation energies, and atomization energies of small main group molecules. Two revised versions of the Perdew–Burke–Ernzerhof (PBE) functional, namely the RPBE and revPBE functionals, widely used for catalysis, do improve the performance of PBE against the two diverse databases, but give worse results than B3LYP (which denotes the combination of Becke's 3-parameter hybrid treatment with Lee–Yang–Parr correlation functional). Our results show that the Minnesota functionals, M05, M06, and M06-L give the best performance for the two diverse databases, which suggests that they deserve more attention for applications to catalysis. We also obtain notably good performance with the tauHCTHhyb, B97X-D, and MOHLYP functionals (where MOHLYP denotes the combination of the OptX exchange functional as modified by Schultz, Zhao, and Truhlar with half of the LYP correlation functional).

877. "Density Functional Study of CO and NO Adsorption on Ni-Doped MgO(100)," R. Valero, J. R. B. Gomes, D. G. Truhlar, and F. Illas, Journal of Chemical Physics **132**, 104701/1-13 (2010).

> The adsorption of small molecules such as NO or CO on surfaces of magnetic oxides containing transition metals is difficult to model by current density functional approximations. Two such oxides are NiO(100) and Ni-doped MgO(100). Here we compare the results of a theoretical model of the Ni-doped MgO(100) surface with experimental results on NiO(100), which introduces some uncertainty into a quantitative theory–experiment comparison. In the present work, we tested seven meta-GGA and hybrid meta-GGA functionals, in particular, three developed by the Minnesota group (M05, M06-L, and M06), and four developed elsewhere (TPSS, TPSSh, TPSSKCIS, and B1B95); six GGA functionals, including BP86, PBE, and four other functionals that are modifications of PBE (PBEsol, SOGGA, revPBE, and RPBE); five hybrid GGA functionals (B3LYP, PBE0, B97–2, B97–3, and MPWLYP1M); and one unconventional functional of the generalized gradient type with scaled correlation called MOHLYP. The Minnesota meta-GGA functionals were found in the past to be very good choices when transition metal atoms were present; the other functionals chosen are a selection from the most currently used and most promising sets of functionals for bulk solids and surfaces and for transition metals. The difficulty is due to the charge transfer between open shells in the case of NO and to the weak character of the interaction in the case of CO. It is shown that the M06 hybrid meta functional applied to NO or CO on a model of the Ni-

doped MgO(100) surface is able to provide a good description of both adsorbate geometries and binding energies. The M06 vibrational frequency shifts are more accurate than for other functionals, but there is still room for improvement.

881. "Binding Energy of d^{10} Transition Metals to Alkenes by Wave Function Theory and Density Functional Theory," B. B. Averkiev, Y. Zhao, and Donald G. Truhlar, Journal of Molecular Catalysis A **324**, 80-88 (2010). (invited paper for a special issue on Computational Catalysis, edited by P.O. Norrby and G. C. Lloyd-Jones) dx.doi.org/10.1016/j.molcata.2010.03.016

The structures of $Pd(PH_3)_2$ and $Pt(PH_3)_2$ complexes with ethene and conjugated C_nH_{n+2} systems (n = 4, 6, 8, and 10) were studied. Their binding energies were calculated using both wave function theory (WFT) and density functional theory (DFT). Previously it was reported that the binding energy of the alkene to the transition metal does not depend strongly on the size of the conjugated C_nH_{n+2} ligand, but that DFT methods systematically underestimate the binding energy more and more significantly as the size of the conjugated system is increased. Our results show that recently developed density functionals predict the binding energy for these systems much more accurately. New benchmark calculations carried out by the coupled cluster method based on Brueckner orbitals with double excitations and a quasiperturbative treatment of connected triple excitations (BCCD(T)) with a very large basis set agree even better with the DFT predictions than do the previous best estimates. The mean unsigned error in absolute and relative binding energies of the alkene ligands to $Pd(PH_3)_2$ is 2.5 kcal/mol for the ωB97 and M06 density functionals and 2.9 kcal/mol for the M06-L functional. Adding molecular mechanical damped dispersion yields even smaller mean unsigned errors: 1.3 kcal/mol for the M06-D functional, 1.5 kcal/mol for M06-L-D, and 1.8 kcal/mol for B97-D and ωB97X-D. The Minnesota functionals also lead to improved accuracy for the analogous Pt complexes. These results show that recently developed density functionals may be very useful for studying catalytic systems involving Pd d^{10} centers and alkenes.

882. "Density Functional Calculations of E2 and S_N2 Reactions: Effects of the Choice of Density Functional, Basis Set, and Self-Consistent Iterations," Y. Zhao and D. G. Truhlar, Journal of Chemical Theory and Computation **6**, 1104-1108 (2010).

We have computed stationary points on the potential energy surface for the *anti*-E2, *syn*-E2, and S_N2 pathways of the reactions of F⁻ and Cl⁻ with CH_3CH_2F and CH_3CH_2Cl with fully self-consistent fields and Gaussian basis functions. We find large differences from previously reported [Bento, A. P.; Sola`, M.; Bickelhaupt, F. M. *J. Chem. Theory Comput.* **2008**, *4*, 929] calculations with Slater-type orbitals. We revise the findings of the previous study; in particular, we find average absolute errors in kcal/mol compared to benchmark calculations of 20 stationary point energies (6 saddle points and 14 minima) of 0.9 for M06-2X, 1.2 for M08-SO, 1.4 for M06-HF, 2.0 for M06, 2.3 for B3LYP, 2.5 for OLYP, 2.7 for M06-L, and 3.5 kcal/mol for TPSS. We also compare the predictions of various density functionals for the partial atomic charges at the transition states.

892. "Including Charge Penetration Effects in Molecular Modeling," B. Wang and D. G. Truhlar, Journal of Chemical Theory and Computation **6**, 3330-3342 (2010). dx.doi.org/10

Electrostatic effects are often the dominant component of intermolecular

interactions, but they are often modeled without accounting for charge penetration effects due to the finite extent of electronic orbitals. Here, we propose a new scheme to include charge penetration effects in electrostatic modeling, and we parametrize it and illustrate it by employing the electronically embedded combined quantum mechanical and molecular mechanical (QM/MM) method. It can also be extended to other molecular modeling approximations that include electrostatic effects. The method, which is based on introduction of a single parameter for each element, is simple in concept and implementation, modest in cost, and easily incorporated into existing codes. In the new scheme, the MM atomic charge density of an atom in a molecule is represented by a screened charge rather than by a point charge. The screened charge includes a point charge for the nucleus, core electrons, and inner valence electrons, and a smeared charge for the outer valence electron density, which is distributed in a Slater-type orbital representing the outer part of the atomic charge distribution such that the resulting pairwise interactions are still analytic central potentials. We optimize the exponential parameters of the Slater-type orbitals for 10 elements, in particular H, C, N, O, F, Si, P, S, Cl, and Br, to minimize the mean unsigned error (MUE) of the QM/MM electrostatic and induction energies with respect to the Hartree-Fock electrostatic energies and the sum of induction and induction-exchange energies calculated by symmetry-adapted perturbation theory (SAPT). The resulting optimized exponential parameters are very physical, which allows one to assign parameters to all nonmetal elements (except rare gases) with atomic number less than or equal to 35. For a test set of complexes, the improved description of MM charge densities reduces the error of electrostatic interactions between QM and MM regions in the QM/MM method from 8.1 to 2.8 kcal/mol and reduces the error of induction interactions from 1.9 to 1.4 kcal/mol.

893. "Metal-Organic Charge Transfer Can Produce Biradical States and is Mediated by Conical Intersections," O. Tishchenko, R. Li, and D. G. Truhlar, Proceedings of the National Academy of Sciences of the United States of America **107**, 19139-19145 (2010). dx.doi.org/10.1073/pnas.1010287107

This paper illustrates key features of charge transfer between calcium atoms and prototype conjugated hydrocarbons (ethylene, benzene, and coronene) as elucidated by electronic structure calculations. One- and two-electron charge transfer is controlled by two sequential conical intersections. The two lowest electronic states that undergo a conical intersection have closed-shell and open-shell dominant configurations correlating with the $4s_2$ and $4s_1 3d_1$ states of Ca, respectively. Unlike the neutral–ionic state crossing in, for example, hydrogen halides or alkali halides, the path from separated reactants to the conical intersection region is uphill and the charge-transferred state is a biradical. The lowest-energy adiabatic singlet state shows at least two minima along a single approach path of Ca to the π system: (i) a van der Waals complex with a doubly occupied highest molecular orbital and a small negative charge on Ca and (ii) an open-shell singlet (biradical) at intermediate approach (Ca···C distance ≈2.5–2.7 Å) with molecular orbital structure $\phi_1 \phi_2$, where ϕ_2 is an orbital showing significant charge transfer form Ca to the π-system, leading to a one-electron multicentered bond. A third minimum (iii) at shorter distances along the same path corresponding to a closed-shell state has also been found; however, it does not necessarily represent the ground state at a given Ca···C distance in all three

systems. The topography of the lowest adiabatic singlet potential energy surface is due to the one- and two-electron bonding patterns in Ca–π complexes.

894. "Adequate Representation of Charge Polarization Effects Leads to a Successful Treatment of the $CF_4 + SiCl_4 \rightarrow CCl_4 + SiF_4$ Reaction by Density Functional Theory," R. Li, Y. Zhao, and D. G. Truhlar, Chemical Communications, 47, 2357-2359 (2011). dx.doi.org/10.1039/C0CC02845B, Communication.

Adequate polarization functions reduce the error of density functional theory (DFT) for the heat of reaction for $CF_4 + SiCl_4$ from 9–12 kcal/mol to 2–4 kcal/mol, and using an improved density functional further reduces it to 1 kcal/mol. This reaction was previously identified as a stumbling block for DFT, but we show that the problem with the previous calculations was not DFT but rather inadequate basis sets to account for intramolecular charge polarization.

897. "Minimally Augmented Karlsruhe Basis Sets," J. Zheng, X. Xu, and D. G. Truhlar, Theoretical Chemistry Accounts **128**, 295-305 (2011). dx.doi.org/10. 1007/s00214-010-0846-z

We propose an extension of the basis sets proposed by Ahlrichs and coworkers at Karlsruhe (these basis sets are designated as the second-generation default or "def2" basis sets in the Turbomole program). The Karlsruhe basis sets are very appealing because they constitute balanced and economical basis sets of graded quality from partially polarized double zeta to heavily polarized quadruple zeta for all elements up to radon ($Z = 86$). The extension consists of adding a minimal set of diffuse functions to a subset of the elements. This yields basis sets labeled minimally augmented or with "ma" as a prefix. We find that diffuse functions are not quite as important for the def2 basis sets as they are for Pople basis sets, but they are still necessary for good results on barrier heights and electron affinities. We provide assessments and validations of this extension for a variety of data sets and representative cases. We recommend the new ma-TZVP basis set for general-purpose applications of density functional theory.

900. "Applications and Validations of the Minnesota Density Functionals," Y. Zhao and D. G. Truhlar, Chemical Physics Letters **502**, 1-13 (2011). (Frontiers Article)

We discuss and review selected recent applications and validations of the Minnesota density functionals, especially the M06 family, emphasizing nanochemistry, organic, inorganic, and biological chemistry, and catalysis and highlighting the broad accuracy of these functionals as compared to previous popular functionals for thermochemistry, kinetics, and noncovalent interactions.

905. "Density Functional Theory for Reaction Energies. Test of Meta and Hybrid Meta Functionals, Range-Separated Functionals, and Other High-Performance Functionals," Y. Zhao and D. G. Truhlar, Journal of Chemical Theory and Computation, published online Feb. 3, 2011 (Articles ASAP). dx.doi.org/10.1021/ct1006604

The present study compares the accuracy of 30 density functionals for four databases of reaction energies studied recently by Grimme and co-workers. For 20 of the density functionals, the calculations are new, and the calculations are compared to previous work for the other 10. We present the results in detail for 11 of the functionals and as mean unsigned errors for the others. The results presented in detail are for the seven most recent Minnesota functionals (M05-2X, M06-L, M06-HF, M06, M06-2X, M08-HX, and M08-SO), three range-separated functionals (HSE, LC-ωPBE, and ωB97X-D), and one dispersion-corrected global

hybrid generalized gradient approximation (B97-D); the other functionals include five dispersion-corrected functionals and their uncorrected analogs, eight high-performing functionals on a recent catalytic-energies test, and the TPSSh functional because it is of special interest to compare its performance to that of M08-SO. Three of the four databases contain a total of 21 rearrangement reaction energies and 13 diverse dissociation or association energies, and the fourth contains three dissociation reaction energies of alkali metal clusters and three dissociation reaction energies of alkali-metal-cation-benzene complexes. The results are especially promising for the Minnesota hybrid meta-GGA functionals and the ωB97X-D, B2PLYP-D, and HSE functionals.

909. "How Accurate are Electronic Structure Methods for Actinoid Chemistry?" B. B. Averkiev, M. Mantina, R. Valero, I. Infante, A. Kovacs, D. G. Truhlar, and L. Gagliardi, Theoretical Chemistry Accounts, in press. (to be published in a memorial issue dedicated to Bjoern Roos)

The CASPT2, CCSD, and CCSD(T) levels of wave function theory and seven density functionals were tested against experiment for predicting the ionization potentials and bond dissociation energies of actinoid monoxides and dioxides with their cations. The goal is to guide future work by enabling the choice of an appropriate method when performing calculations on actinoid-containing systems. We found that four density functionals, namely, MPW3LYP, B3LYP, M05, and M06, and three levels of wave function theory, namely CASPT2, CCSD, and CCSD(T), give similar mean unsigned errors for actinoid–oxygen bond energies and for ionization potentials of actinoid oxides and their cations.

C83. "The Minnesota Density Functionals and Their Applications to Problems in Mineralogy and Geochemistry," Y. Zhao and D. G. Truhlar, in Theoretical and Computational Methods, in Mineral Physics: Geophysical Applications, edited by R. Wentzcovitch and L. Stixrude (Reviews in Mineralogy and Geochemistry, Volume 71, Mineralogical Society of America, Chantilly, VA, 2010), pages 19-37. DOI: 10.2138/rmg.2010.71.2

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.