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Final Report
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Theoretical Modeling of Catalytic processes: Hydrocarbon oxidation and
cracking.

Anthony K. Rappé
Department of Chemistry
Colorado State University

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A. Accomplishment(s) during past year

During the past year we have implemented and have begun validating a new procedure for obtaining partial charge distributions for use in molecular mechanics as well as for use in other methodologies that require a rapid charge estimation procedure. The new procedure is called QEq2. In addition, we have formulated a way of estimating resonance energies within molecular mechanics. This will permit screening transition state energetics as well as transition state structures for reactions involving zeolites and hydrocarbon oxidation. Finally, during the past year, in collaboration with Tom Russo and Rich Martin we have begun an assessment of which of a variety of ab initio electronic structure methods can reproduce the known energetics of the reactions between hydrocarbons and metal oxo complexes.

B. Summary report

The major developments in the past year (QEq2, resonance, and the "validation" of ab initio electronic structure methodologies) are summarized below.

QEq2.

In order to understand the role that a zeolite lattice plays in controlling the catalytic cracking product distribution we previously studied the charge redistribution that occurred for hydrocarbons when they were placed in a zeolite Y supercage using the QEq charge estimation procedure. We found ground state hydrocarbons to be unperturbed by the field provided by the lattice but that a model transition state for the hydride transfer step of the cracking chain reaction was significantly perturbed by the lattice. This difference was attributed to the hydride transfer transition state being larger and hence bulkier than the ground state reactants---not an unexpected result. However, we also found unrealistic degrees of charge transfer between the zeolite and the hydrocarbons using QEq. This and the relative slowness of QEq led to the development of QEq2 summarized below.

A major remaining weakness underlying current molecular simulation methodologies is the treatment of electrostatics. Current approaches predominantly employ fixed charge distributions and further, generally use an electrostatic moment expansion truncated to either monopoles or dipole moments. While the use of these approximations has led to numerous useful results, improved methodologies are certainly needed.

Fundamentally, the fixed charge approximation is an *anti*Born-Oppenheimer approximation. Because of the disparate mass scales electrons, to a good approximation, move adiabatically in the field of "fixed" nuclei. Within the fixed charge model of molecular mechanics and dynamics, electron distributions are assigned, the electron distributions are compressed to point partial electrons, and the point partial electrons are attached to their respective nuclei and held fixed or frozen while the nuclei move.

In addition, electrons are quantum mechanical particles which must be described in terms of density distributions rather than having defined positions in space. Electron densities can be penetrated by nuclei or other electron distributions causing the magnitude of the "charge" seen to

vary with distance.

Because molecular mechanics and molecular dynamics procedures are heavily parameterized the defects associated with using classical electrons can be buried into parameterization procedures to yield useful results. The difficulty in this approach rests in generalization, the parameters are only useful for a limited range of molecular systems and are only useful over a limited span of distance space.

The flow of electrons from one center in a molecule to another has been an important concept in chemistry from the 1930's. The concept of electronegativity was developed to describe this effect. QEq, the electronegativity equilization method (EEM) and QEq2 use Sanderson's concept that as atoms are brought together electrons will flow within a molecule until electron equilibrium has been reestablished. Electronegativities, higher order electrostatic derivatives, and off-center electrostatic effects are used to govern the degree of electron flow. In QEq2 the parameters χ and J_{A0} are obtained from IP's and EA's from equations (1) and (2)

$$\left(\frac{\partial E}{\partial Q}\right)_{A0} + \frac{1}{6}\left(\frac{\partial^3 E}{\partial Q^3}\right)_{A0} = \frac{IP_A + EA_A}{2} \quad (1)$$

$$\frac{1}{2}\left(\frac{\partial^2 E}{\partial Q^2}\right)_{A0} = \frac{IP_A - EA_A}{2} \quad (2)$$

where $\left(\frac{\partial E}{\partial Q}\right)_{A0}$ is the electronegativity χ and $\left(\frac{\partial^2 E}{\partial Q^2}\right)_{A0}$ is J_{A0} , the self-coulomb integral. The cubic term $\frac{1}{6}\left(\frac{\partial^3 E}{\partial Q^3}\right)_{A0}$ is folded into J_{A0} by making it charge dependent, J_{AQ} , see Equation (3).

$$J_{AQ} = J_{A0} + \gamma Q \quad (3)$$

The proportionality constant γ has been adjusted to reproduce the dipole moments of H_2O and NH_3 , yielding a final value of 0.5.

Because of electron cloud penetration effects, coulombic interactions involving electrons are not properly described in terms of $1/R$. For a pair of hydrogen atoms the two center coulomb integral, $J_{I\Gamma}$, deviates from $1/R$ significantly at 3 Å, see Equation (4).

$$J_{I\Gamma} = \zeta \left\{ \frac{1}{\zeta R} - e^{-2\zeta R} \left(\frac{1}{\zeta R} + \frac{11}{8} + \frac{3}{4}\zeta R + \frac{1}{6}\zeta^2 R^2 \right) \right\} \quad (4)$$

In QEq and QEq2, electrostatic interactions are described by these $J_{I\Gamma}$ coulomb integrals. In QEq the Slater exponents ζ were a third parameter, in addition to the electronegativities and J_{A0} 's. Here we obtain ζ from J_{A0} . Since $J_{I\Gamma}$ should yield J_{A0} when $R \rightarrow 0$ in QEq2 ζ is obtained from J_{A0} since $J_{I\Gamma}$ at $R = 0$ is $\frac{5}{8}\zeta$, see Equation (5).

$$\zeta_A = \frac{8}{5} J_{A0} \quad (5)$$

The exponents for mixed ζ integrals are taken directly from the $J_{I\Gamma}$ equation, see Equation (6).

$$\zeta_{AB} = \frac{1}{2} (\zeta_A + \zeta_B) (1 - \tau^2) (1 - \frac{\tau^2}{5}) \quad (6)$$

The τ in Equation (6) is given by Equation (7).

$$\tau = \frac{(\zeta_A - \zeta_B)}{(\zeta_A + \zeta_B)} \quad (7)$$

When discussing magnitudes of intermolecular interactions charge-charge or dipole-dipole interactions are considered largest, charge or dipole-induced dipole or polarization effects second largest, and induced dipole-induced dipole or dispersion interactions smallest. In molecular mechanics and dynamics charge-charge interactions and induced dipole-induced dipole interactions are usually included but the comparably important charge-induced dipole interactions are ignored or approximately folded into the overall parameterization. In QEq and EEM the effects of bond polarization were explicitly included in the model but the polarization of lone pair electron density was not treated. Since the induced dipole portion of a charge-induced dipole term is dependent upon all of the centers in a molecular system the coordinate derivatives of an induced dipole term will grow as the number of centers to the third power. This makes inclusion of such a term computationally unattractive.

The shell model is a less demanding alternative to a proper charge-induced dipole term. It has been successfully used in studies on inorganic materials and piezoelectric polymers. In the conventional shell model atoms or ions are described in terms of nuclear cores and massless shells of electron density. The shells and cores are connected by harmonic potentials, the force constants of which are related to the electric polarizabilities of the free atoms or ions. Primary difficulties with the shell model include the need for additional parameters and the fact that the proper interaction between an electron density and its nucleus is not harmonic.

In QEq2 a quantum mechanical shell model is used for lone pair electron densities. That is, rather than using a parameterized harmonic potential, Equation (4) is used to describe electron nuclear attraction with ζ obtained from Equation (5). The number of lone pair electrons on an atomic center is based on the number of non-bonded electrons on that center. For example, oxygen in H_2O has four lone pair electrons and nitrogen in NH_3 has two lone pair electrons. For centers with lone pairs the nuclear position is assigned a positive charge of the same magnitude as the number of lone pair electrons. Because lone pairs are electron densities van der Waals interactions are included at the lone pair positions. The van der Waals term between a lone pair and its nucleus are ignored but terms between a lone pair and other nuclei and lone pairs are included. Conventional atomic van der Waals terms are partitioned between the lone pair positions and the nuclear positions based on the number of electrons in bond pairs and in lone pairs. For example, since H_2O is a closed shell molecule the oxygen has eight valence electrons, four in bond pairs and four in lone pairs. Fifty percent of the electron density is associated with bonding electrons and fifty percent with lone pair electrons. Half of the oxygen van der Waals interaction is located at the nuclear position and half at the lone pair position. This is accomplished by halving the conventional atomic oxygen van der Waals well depth, ϵ , and evaluating van der Waals interactions for both nuclear and lone pair positions. For NH_3 , again a closed shell molecule, 25% of the

electron density is associated with lone pairs and 75% with bond pairs. The nitrogen lone pair van der Waals well depth used is $\frac{1}{4}$ the conventional atomic ϵ and the nitrogen nuclear van der Waals well depth is $\frac{3}{4}$ the conventional atomic ϵ .

In QEq and EEM partial charges are found by equating chemical potentials and applying the constraint that the sum partial charges is equal to the net charge of the molecular system. In order to increase the computational speed of the method and more tightly define the locations of electron densities additional constraints have been added to QEq2. In QEq2 a valence bond bonding model is adopted: electron densities are confined to bond pairs, lone pairs, or delocalized sets of electron density. Within a bond pair, electron density flows to equilibrate the chemical potentials of the bonded centers in the field of the full electrostatic model. Lone pairs of electrons move in the electrostatic and van der Waals field of the other atoms and lone pairs. Delocalized sets of electron density such as in a block of metal are treated as in QEq. The QEq2 molecular electrostatic energy expression is given in Equation (8).

$$\begin{aligned}
 E_Q = & \sum_i^n (Q_i \chi_i + \frac{1}{2} \sum_j^n Q_i Q_j J_{ij}) \\
 & + \sum_i^n \sum_{\substack{j=1 \\ j \neq \bar{i}}}^m Q_i N_j (J_{i\bar{j}} - J_{ij}) + \text{vdW}_{ij} \\
 & + \sum_i^m \sum_{j=i+1}^m N_i N_j (J_{ij} - J_{i\bar{j}} - J_{\bar{i}j} + J_{\bar{i}\bar{j}}) + \text{vdW}_{ij}
 \end{aligned} \quad (8)$$

In Equation (8) n is the number of atoms, m is the number of lone pairs, and $\bar{i}$ indicates the nuclear position associated with lone pair i . J_{ij} is the charge dependent coulombic interaction discussed in section II.d and vdW_{ij} is the van der Waals interaction. In QEq2 a Morse-van der Waals potential is used. The functional form is given in Equation (9).

$$E_{MV} = D_e [e^{-2\alpha(r-r_e)} - 2e^{-\alpha(r-r_e)}] \text{ for } r < r_{\text{cut}}$$

$$E_{MV} = \frac{-C_6}{r^6} \text{ for } r > r_{\text{cut}} \quad (9)$$

$$(C_6 \text{ and } r_{\text{cut}} \text{ set so } E_{MV} \text{ and } \frac{\partial E}{\partial r} \text{ match at } r = r_{\text{cut}})$$

Q_i is the total partial charge on center i given by Equation (10). N_i is the number of lone pair electrons on center i .

$$Q_i = Q_i^{\text{net}} + \sum_k^{b_i} q_k^i \quad (10)$$

In Equation (10) b_i is the number of bonds to center i , q_k^i is the coefficient for the partial charge density on center i associated with bond k , and Q_i^{net} is the net or formal charge associated with center i . In QEq the first line of Equation (8) was differentiated with respect to Q_i and the resulting set of n equations (plus the charge conservation constraint) solved for the Q_i 's. In QEq2 bond partial charge densities, q_k^i , and lone pair coordinates are determined. The bond partial charge densities are determined by differentiating Equation (8) with respect to q_k^i including $\frac{\partial J_{ij}}{\partial q_k^i}$ terms, equating intrabond chemical potentials, and constraining bond pairs to two electrons. The lone pair coordinate positions are optimized in a fixed partial charge field. Since the bond partial charge densities and lone pair positions are interdependent an iterative sequence is repeated until the energy change drops below a threshold.

In molecular mechanics assigning partial charge distributions to small molecules such as HF, H₂O, and NH₃ is problematic. If the *ab initio* electrostatic potential (ESP) is fit the computed, partial charge based, dipole moment is substantially in error—it is too large. If the dipole moment is fit the charges are too small. Because nearest neighbors "see" the partial charge distribution and centers far away "see" the dipole both sets of interactions are important in molecular mechanics and dynamics. Four-site H₂O models have been developed for this purpose, but where the fourth center is placed is arbitrary, often the center of mass is used. In QEq2 a four site H₂O model arises naturally—the lone pair position is optimized and moves off the nuclear position due to an attraction to the partially positive hydrogen centers.

QEq2, Hartree Fock, QCISD(T), and experimental dipole moments are collected in Table 1. As is generally recognized *ab initio* Hartree Fock and QCISD(T) dipole moments are too large. QEq2 matches experiment. The importance of the lone pair center can be seen from the partial charges reported in Table 2. Fitting atom centered partial charges to the experimental dipole moment, e.g. a three-site model for H₂O, yields charges smaller than are conventionally used in condensed state H₂O simulations and smaller than obtained by fitting the *ab initio* ESP.

QEq2, and *ab initio* ESP partial charges for zeolite models O(SiH₃)₂ and Si(OH)₄ are collected in Table III. Given the range of results obtained by *ab initio* electronic structure the preliminary QEq2 results are quite encouraging.

Resonance.

Be it an external metal oxide surface or the interior surface of a zeolite, as one moves from methane to larger hydrocarbons the surface provides a steric block to direct reactivity. For example, if one considers the hydride transfer step of a carbenium ion carrier hydrocarbon cracking process, the carbenium ion can either be bound to the metal oxide surface, (1) or present as a free species, (2). If the carbenium ion is bound to the surface it is difficult to construct a model of the

hydride transfer step since the surface will block the backside of the carbenium ion. This suggests that a detailed description of a carbenium ion carrying chain mechanism for hydrocarbon cracking would involve bound carbenium ions (1), in equilibrium with reactive free carbenium ions, (2). This makes computationally modeling such processes problematic. The theoretical methodology used must be able to treat (1) and (2) with equal accuracy. In order to study the steric role that the surface plays must use a large cluster or the infinite system itself. This suggests that molecular mechanics should be used in conjunction with electronic structure techniques.

Unfortunately, in standard, conventional molecular mechanics one assigns hybridizations, bonds and partial charges which remain fixed during a simulation. Comparisons between species with differing hybridizations, bonds, and partial charges is simply not possible. For example, consider NaCl. If one draws a bond between the Na and the Cl then the NaCl will correctly dissociate to Na and Cl atoms at long R in the gas phase, but because electrostatic interactions between the Na and Cl are ignored the NaCl will not dissociate to Na⁺ and Cl⁻ in solution (or in a zeolite lattice). If one does not draw the bond but instead describes the interaction as Na⁺Cl⁻ using electrostatic attraction and van der Waals repulsion to form the "bond" then dissociation in solution (or in a zeolite lattice) will occur properly but the molecule will not dissociate to Na and Cl atoms in the gas phase (the ionization energy of Na and the electron affinity of Cl are not in the model). If one knows the answer for a particular system it can be modeled but if one wants to use molecular mechanics to help determine the answer there are problems.

One solution to this problem is to simultaneously use a covalent model and an ionic model and let the geometry and environment determine the proper partitioning between models. This can be accomplished using a valence bond model of bonding, Equation (11),

$$E_{\text{bond}} = \lambda_{\text{cov}}^2 E_{\text{cov}} + \lambda_{\text{ionic}}^2 E_{\text{ionic}} + 2\lambda_{\text{cov}}\lambda_{\text{ionic}} E^{\text{x}}_{\text{cov,ionic}} \quad (11)$$

where E_{cov} and E_{ionic} are molecular mechanics representations of covalent and ionic bonding and $E^{\text{x}}_{\text{cov,ionic}}$ is the interaction between the two. The λ 's variationally determined through the solution of a 2x2 determinant.

A related problem arises when one looks at cracking hydride exchange transition states. Using Gaussian 92, Komala Krishnaswamy found the exchange "transition state" for secondary transfer from propane to propyl cation, (3), to be a transition state or saddle point (a single imaginary vibrational frequency). The analogous structure for methane plus methyl cation, (4), is a ground or stationary state with a binding energy of roughly 35 kcal/mol. By molecular mechanics both (isopropyl and methyl) cases are "transition states" if the reactant and product structures are not allowed to interact. As with simultaneously using covalent and ionic models this "interaction" can occur if a valence bond model of bonding is used, Equation (12),

$$E_{\text{bond}} = \lambda_{\text{r}}^2 E_{\text{r}} + \lambda_{\text{p}}^2 E_{\text{p}} + 2\lambda_{\text{r}}\lambda_{\text{p}} E^{\text{x}}_{\text{r,p}} \quad (12)$$

where E_r and E_p and molecular mechanics representations of reactant, or first structure and product, or second structure and $E_{r,p}^x$ is the interaction between the two. Again, the λ 's can be variationally determined through the solution of a 2x2 determinant.

The difficulty is determining the interaction or exchange terms $E_{cov,ionic}^x$ and $E_{r,p}^x$. We, in the past, have used a simplified cross term due to Jensen, see Equation (13), to test whether or not molecular mechanics could reproduce transition state structures.

$$E = \frac{1}{2}E_r + \frac{1}{2}E_p + \frac{(E_r - E_p)^2}{E_{denom}} \quad (13)$$

Molecular mechanics results (and in parentheses ab initio results) on the Diels-Alder reaction of butadiene plus ethylene, the Cope rearrangement of 1,5 hexadiene, and a H-D exchange transition state for zeolite cluster model are presented in Figures 1-3. The geometric results are quite encouraging.

In the past year we have formulated a solution to the cross term problem that may be general---we need to test it for a variety of reactions including the cracking hydride transfer reaction. Within a simple valence bond framework the energy of a molecular system can be written in terms of coulombic interactions or integrals, Q , and exchange interactions or integrals, K . By equating combinations of Q and K terms with molecular mechanics non-bonding and bonding potential functions, respectively, a general expression for $E_{r,p}^x$ has been obtained. In BEBO and for LEPS surfaces the non-bond curve arises from a anti-Morse function. The molecular mechanics non-bond potential provides a more precise representation of this interaction. To date the only case we have studied is benzene. In molecular mechanics benzene is typically treated with a single energy expression and bond orders of $1\frac{1}{2}$ between the carbons. An alternative description would be based on two cyclohexatriene structures, (5), which resonantly interact to generate the symmetric, observed benzene structure. This provides a model resonant case where the answer is fairly well known. Using molecular mechanics, the distortional energy from the 3 double bond, 3 single bond form to the symmetric form is 11 kcal/mol, see (6). With the initial form for the exchange term the resonance stabilization energy is 19 kcal/mol, see (7), leading to a reasonable estimate for the "resonance energy" of benzene at 8 kcal/mol, see (8). Even though the resonance energy of benzene is underestimated a symmetric structure was found. Improvements in the description of the cross term should yield a method to study cracking transition states and permit the dynamic distortion from covalent to ionic structures.

Re-O Thermodynamic validation

During the past year we, in collaboration with Tom Russo and Rich Martin of Los Alamos have assessed which of a variety of ab initio electronic structure methods can reproduce the known

energetics of the reaction between a hydrocarbon and a metal oxo complex. In past reports we have discussed difficulties in obtaining reasonable ground and transition state structures and energetics for reactions involving metal oxygen bonds. A significant problem is the lack of validation data. Either significant overoxidation is observed, making measurements of reaction exothermicities problematic or the solvent is water making solvation effects substantial. A reasonable benchmark reaction is shown in Figure 4. The exothermicity is known for a number of olefins and the reaction is carried out in nonpolar solvent. The ab initio exothermicities we have obtained are collected in Table IV. The systems studied include the observed pentamethyl cyclopentadienyl rhenium trioxo system (Cp^*ReO_3), a model system wherein the Cp^* is replaced by the smaller cyclopentadienyl ligand (Cp) and a further simplified system wherein the Cp^* is replaced by a chlorine ligand. Experimentally, for ethylene as the olefin the reaction is nearly thermal neutral. Clearly none of the conventional approaches tried is satisfactory. Density functional results by Russo and Martin are significantly more encouraging.

Table I Dipole Moments (debye)

Compound	<i>Ab initio</i> ^a			Experiment
	QEq2	HF	QCISD	
HF	1.84	2.07	1.98	1.826 ^b (0.917Å) ^b
H ₂ O	1.83	2.18	2.09	1.85 ^c (0.957Å, 104.51°) ^d
NH ₃	1.47	1.89	1.82	1.47 ^c (1.012Å, 106.68°) ^d

^a6-31**G basis^bHuber and Herzberg^cCRC^dLandolt-Börnstein

Table II Hydrogen Charges

Compound	<i>Ab initio</i> ^a			
	QEq2	Mulliken	HF ESP	Experiment (μ)
HF	0.55	0.42	0.46	0.42
H ₂ O	0.45	0.34	0.40	0.33
NH ₃	0.37	0.26	0.34	0.27

Table III Charge Distributions of O(SiH₃)₂ and Si(OH)₄

Compound	Atom	QEq2	CHELPG(6-311G**)	MSK	Mulliken
O(SiH ₃) ₂	O	-1.026	-0.565	-1.298	-0.981
	Si	0.895	0.890	1.187	1.101
	H	-0.128	-0.203	-0.176	-0.198
Si(OH) ₄	O	-0.992	-0.935		-0.711
	Si	2.054	1.763		1.611
	H	0.479	0.494		0.308

Table IV Summary of Oxidation Exothermicities

	Cl	Cp	Cp*
HF	-55	-87	-69
MP2	+52	+37	
QCISD(T)	+11		
PP+Pol(2/1)+RCI(4)	-9	-40

MP2/6-31G* (R. J. Loncharich) in Houk, K. N.; Li, Y.; Evanseck, J. D *Angew. Chem. Int. Ed. Engl.* 31 682 **1992**

Figure 1. Diels-Alder Transition State ab initio results in [].

CASSCF/3-21G	2.086Å
CASSCF/6-31G	2.189Å
CASPT2N/3-21G	1.890Å
CASPT2N/6-31G*	1.745Å
CASPT2N/6-311G**	1.775Å
CASPT2N/6-311G(2d,2p)	1.885Å

Morokuma, K.; Borden, W. T.; Hrovat, D. A. *J. Am. Chem. Soc.* 110, 4474 1988
 Dupuis, M.; Murray, C.; Davidson, E. R. *J. Am. Chem. Soc.* 113, 9746 1991
 Hrovat, D. A.; Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* 116, 1072 1994

Figure 2. Cope Transition State ab initio results in [].

Kramer, G. J.; van Santen, R. A. *JACS* **1995**, *117*, 1766

Barrier SDCl = 37 kcal/mol

Figure 3. Methane H-D exchange transition state and Si-O-Si benchmark results (experiment in ()).

	ΔH_O	ΔH_O^*	ΔH_E^*
ethylene	-.	-.	28.0
2-butene	[-5.2]	-.	30.5
bicyclo[2.2.2]oct-2-ene	-9.7	-.	31.5
norbornene	-10.9	18.2	29.1
norbornadiene	[-13.2]	16.8	-.
<i>trans</i> -cyclooctene	[-14.2]	11.7	-.

Gable, K. P.; Phan, T. N. *J. A. C. S.* **1994** *116*, 833.

Figure 4. Observed enthalpies for the reaction of olefins with Cp^*ReO_3