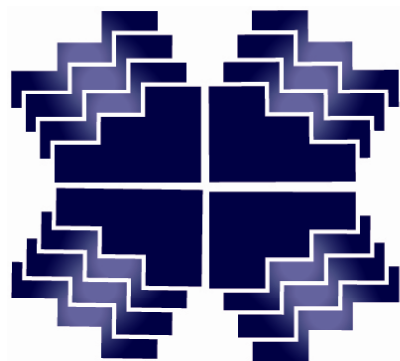


Multiscale Materials Modeling

Lecture 01

Capabilities of Quantum Mechanical Calculations



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Sustainable Technology through
Advanced Interdisciplinary Research

Capabilities of Quantum Mechanical Calculations

- I. What are Quantum Mechanical Calculations?
- II. Applications
 - II.A. Optimized Molecular Structures
 - II.B. Electronic Structure
 - II.C. Thermodynamic Properties
 - II.D. Reaction Pathways and Kinetics
 - II.E. Parameterization of Classical Potentials
- III. Strengths and Weaknesses
 - III.A. Theoretical Limitations
 - III.B. Computational Limitations
- IV. References

What are Quantum Mechanics?

Quantum mechanics is a branch of physics dealing with the behavior of matter and energy on the minute scale of atoms and subatomic particles.

Quantum mechanics is the foundation of several branches of physics, including electromagnetism, particle physics, condensed matter physics, and even parts of cosmology. Quantum mechanics is also essential to the theory of chemical bonding, structural biology, and technologies such as electronics, information technology, and nanotechnology. A century of experiments and of work in applied science has proved quantum mechanics successful and practical.

Quantum mechanics began in the early 20th century, with the groundbreaking work of Max Planck and Niels Bohr. Max Born coined the term "quantum mechanics" in 1924. A major early success of quantum mechanics was its explanation of wave-particle duality, namely how on the sub-atomic level what humans had come to conceptualize as particles have wave-like properties and how what humans have learned to call waves can have particle-like properties.

What is the Schrödinger Equation?

In physics, especially quantum mechanics, the Schrödinger equation is an equation that describes how the quantum state of a physical system changes in time. It is as central to quantum mechanics as Newton's laws are to classical mechanics.

For a general quantum system:

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \hat{H} \Psi(\mathbf{r}, t)$$

where

- i is the **imaginary unit**
- $\Psi(\mathbf{r}, t)$ is the **wave function**, which is the **probability amplitude** for different **configurations** of the system.
- \hbar is the **Reduced Planck's constant** (often normalized to 1 in **natural units**).
- \hat{H} is the **Hamiltonian operator**.

What is the time-independent Schrödinger Equation?



The time-independent Schrödinger equation is an eigenvalue problem.

$$\hat{H}\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$

The Hamiltonian is an operator describing the mechanics of the system.

E is the energy of the system.

$\Psi(\mathbf{r})$ is the wave function of the electron.

The only system for which an analytical solution has been found is the hydrogen atom: 1 proton and 1 electron. All other systems require numerical solution.

The numerical solution of the time-independent Schrödinger equation requires both theoretical approximations and numerical approximations.

Solution of the Schrödinger Equation for hydrogen

The hydrogen atom has an analytical solution.

Energy levels

The energy levels of hydrogen, including [fine structure](#) are given by

$$E_{nj} = \frac{-13.6 \text{ eV}}{n^2} \left(1 + \frac{\alpha^2}{n^2} \left(\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \right)$$

where

α is the [fine-structure constant](#)

Wavefunction

The normalized position [wavefunctions](#), given in [spherical coordinates](#) are:

$$\psi_{n\ell m}(r, \vartheta, \varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} e^{-\rho/2} \rho^\ell L_{n-\ell-1}^{2\ell+1}(\rho) \cdot Y_{\ell m}(\vartheta, \varphi)$$

where:

$$\rho = \frac{2r}{na_0}$$

a_0 is the [Bohr radius](#).

$L_{n-\ell-1}^{2\ell+1}(\rho)$ are the [generalized Laguerre polynomials](#) of degree $n-\ell-1$.

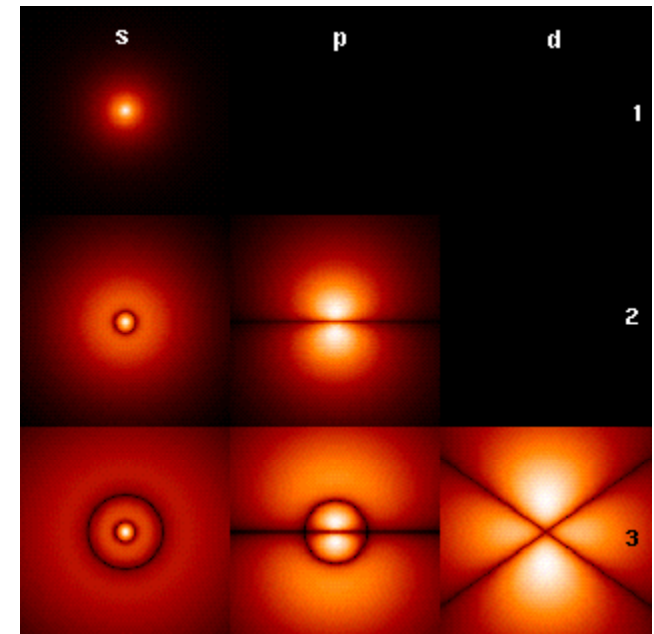
$Y_{\ell m}(\vartheta, \varphi)$ is a [spherical harmonic](#).

The quantum numbers can take the following values:

$$n = 1, 2, 3, \dots$$

$$\ell = n - 1, n - 2, \dots, 1, 0$$

$$m = -\ell, \dots, \ell$$



Probability densities for the electron at different quantum numbers (ℓ , across top, and n , down side)

What is density functional theory?

Density functional theory (DFT) is a quantum mechanical theory used in physics and chemistry to investigate the electronic structure (principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases. With this theory, the properties of a many-electron system can be determined by using functionals, i.e. functions of another function, which in this case is the spatially dependent electron density, $\Psi(\mathbf{r})$. Hence the name density functional theory comes from the use of functionals of the electron density. DFT is among the most popular and versatile methods available in condensed-matter physics, computational physics, and computational chemistry.

The major problem with DFT is that the exact functionals for exchange and correlation are not known except for the free electron gas. However, approximations exist which permit the calculation of certain physical quantities quite accurately. In physics the most widely used approximation is the local-density approximation (LDA), where the functional depends only on the density at the coordinate where the functional is evaluated.

What are basis sets?

A basis set is a mathematical representation of the molecular orbitals within a molecule. The basis set can be interpreted as restricting each electron to a particular region of space. Large basis sets impose fewer constraints, but require more computational resources.

Choice of basis sets change the results. The best basis set to use is not always clear. The biggest is not always the best.

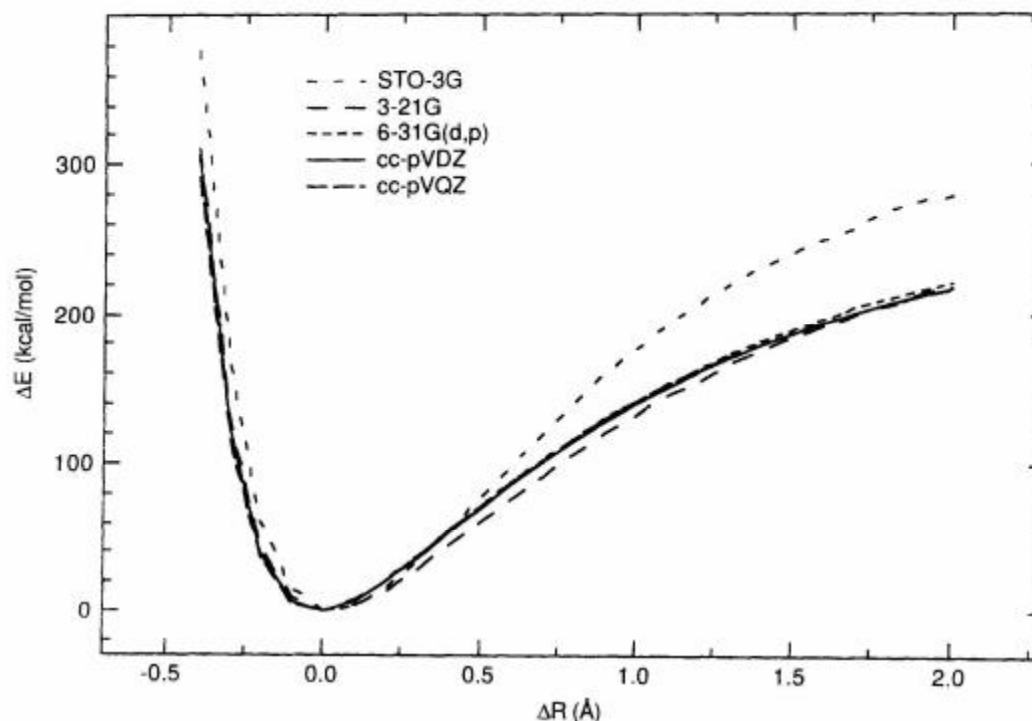


Figure 11.2 Bond dissociation curves for H₂O at the HF level, relative energies

Jensen, F., "Introduction to Computational Chemistry", Second Ed., Wiley & Sons, New York, 1999.

What are quantum mechanical calculations?



For the purposes of this discussion, QM calculations allow you to solve the time-independent Schrödinger equation for the spatial distribution of electrons, using an approximation of the physics (such as Density Functional Theory with a Local Density Approximation) and a numerical approximation of the solution (basis set).

From this solution, many useful properties can be obtained as shown in the following applications.

Capabilities of Quantum Mechanical Calculationsz

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Optimized Molecular Structures



QM calculations can be used to generate the equilibrium or ground state structures of molecules.

The solution of this problem is a set of (x,y,z) coordinates for all atoms in a molecule. The solution is obtained by minimizing the QM energy of the system with respect to the atomic coordinates. As such this is a multivariate nonlinear optimization problem in $3N-6$ dimensions, where N is the number of atoms in the calculation.

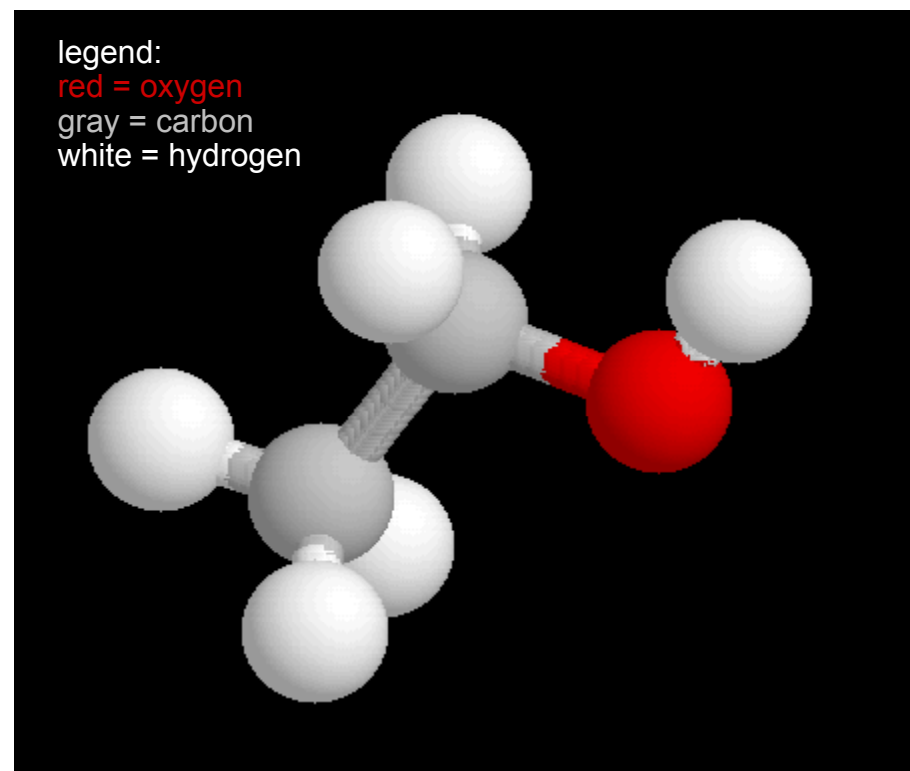
For example, the NIST Chemistry WebBook at <http://webbook.nist.gov/chemistry/> has ground state structures for thousands of molecules, calculated from QM.

Optimized Molecular Structures

The solution of the molecular structure problem is a set of atomic coordinates.

Ethanol ground state from QM.

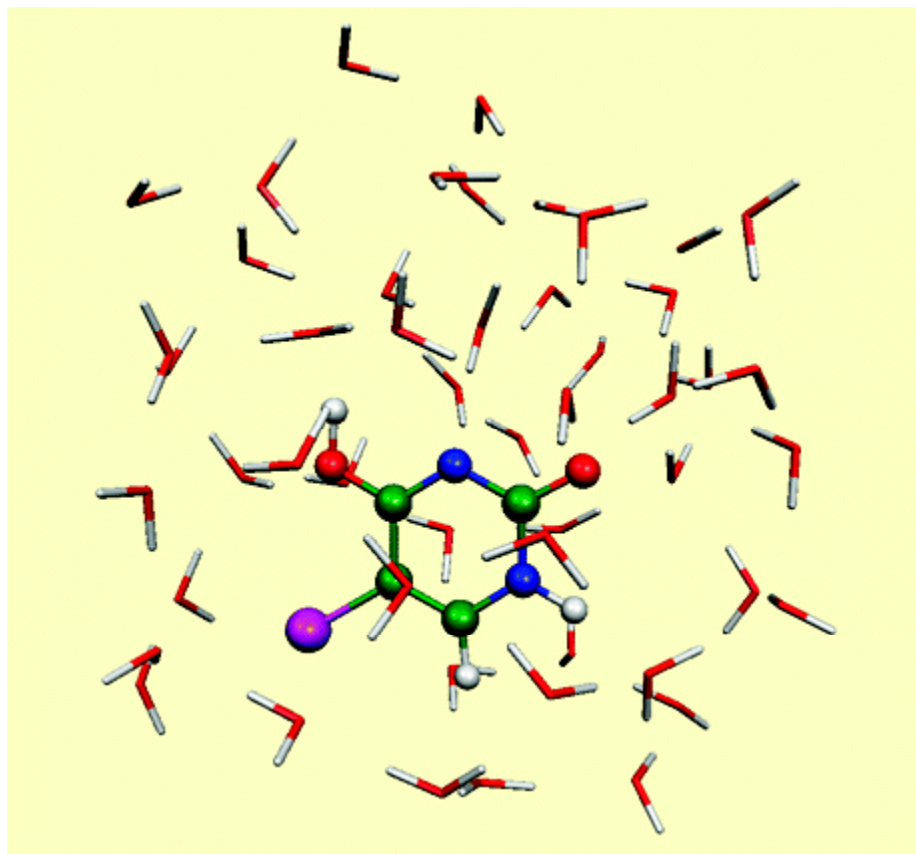
C	1.0303	0.8847	0.9763
C	1.8847	1.9889	1.5717
O	3.1883	1.4807	1.7425
H	0.0000	1.2330	0.8324
H	0.9949	0.0000	1.6255
H	1.4097	0.5558	0.0000
H	1.9050	2.8742	0.9059
H	1.4753	2.3225	2.5456
H	3.7056	2.1820	2.1139



This is the structure one would expect to find if one ethanol molecule were sitting in a vacuum at 0 K. (NIST Chemistry WebBook, <http://webbook.nist.gov/chemistry/>)

Optimized Molecular Structures

It is now becoming possible to do fully quantum calculations of small molecules in the solvated state, i.e. in solution, where the structure may be different that in vacuum.



Density functional theory calculations on the canonical (keto) and rare (enol) tautomeric forms of uracil and 5-bromouracil in a cluster consisting of 50 water molecules are presented. The keto form of uracil is favored over the enol tautomer in both the gas phase and solution. However, the presence of the water cluster reverses the tautomeric preference of 5-bromouracil, rendering the rare tautomeric form to be preferred over the canonical form in aqueous solution. This effect is, to a large extent, due to the more favorable water–water interactions in the cluster around 5-bromouracil and can therefore only be obtained by including explicit water–water interactions in the calculations.

Danilov et al., *J. Phys. Chem. A*, 2009, 113 (11), pp 2233–2235

Optimized Molecular Structures

Quantum mechanics can be used to optimize geometries of biological macromolecules as well, including protein-ligand interactions..

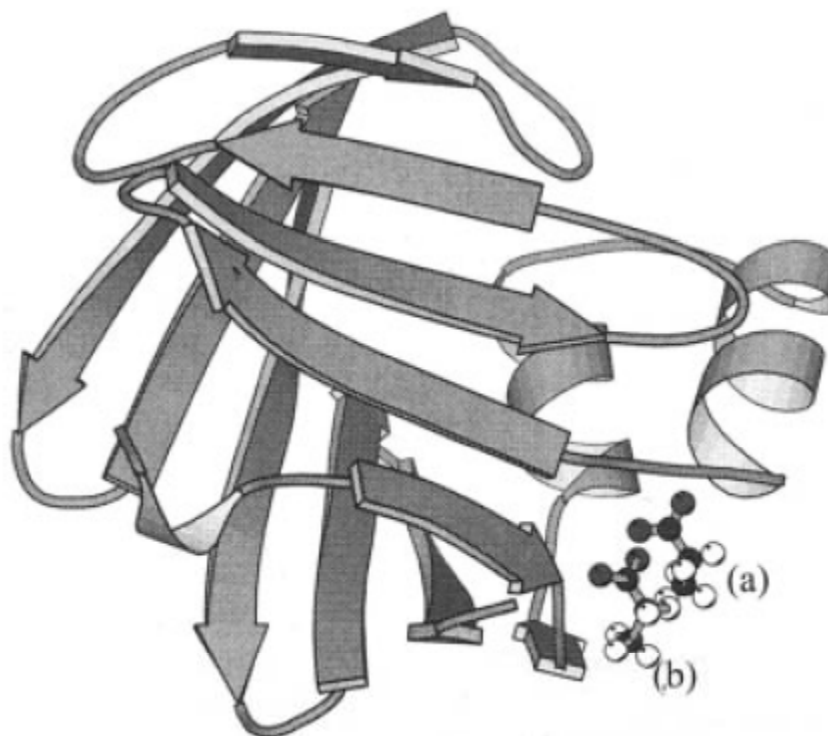
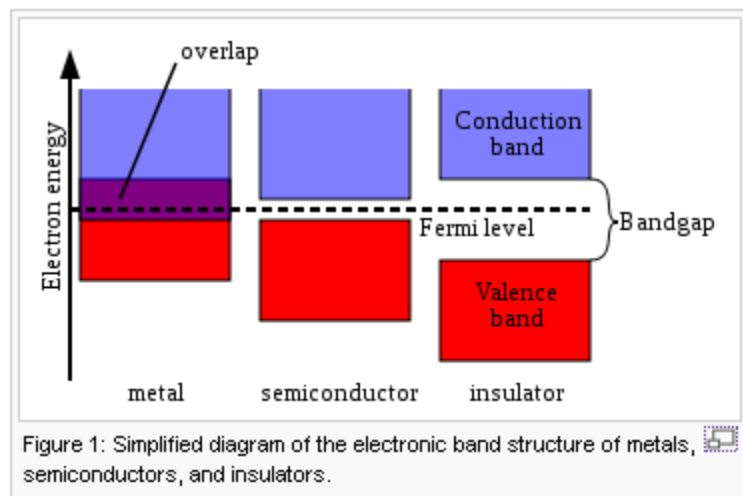


Figure 3. Comparison of crystal structure (a) and optimized structure (b) for the ALBP-propanoic acid binding complex (PDB code: 1LIC).

Xiang, Y., Zhang, D.W., Zhang, J.Z.H., J.Comp. Chem. 2004.

Band-Gap Calculations



The band gap is the energy difference between the valence orbitals bound to a given atom and the conducting orbitals in solids.

Band-Gap for Silica quantum dots as a function of size

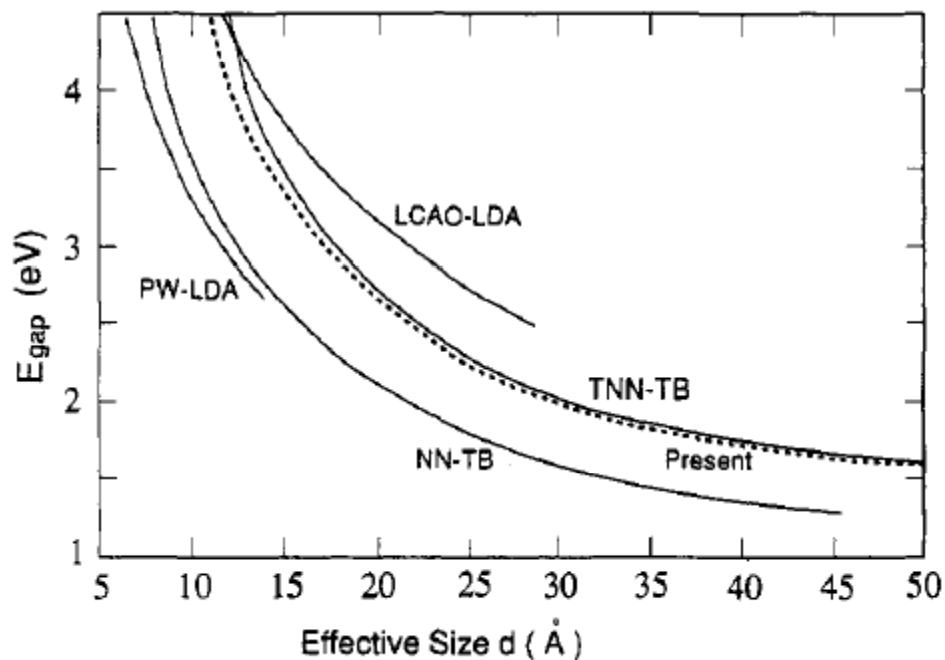


Figure 4. Comparison of calculated LUMO-HOMO gaps *vs* size as obtained with different direct calculation methods. The curve representing the current result is fitted from Figure 2. The results are for PW-LDA,⁴³ NN-TB,⁴⁰ TNN-TB,⁴¹ and LCAO-LDA.⁴² See text for definitions of these methods.

Wang, L.W., Zunger, A., J. Phys. Chem., 1994.

Spectroscopic Properties

Here we show a comparison between experimental and calculated vibrational frequencies of benzene as a function of both method and basis set for benzene.

Benzene experimental, computed and corrected frequencies (cm⁻¹)

Benzene Experimental Freq.	HF						B3LYP						Symmetry Symbol	Pitzer Number Symbol
	6-31G(d)		6-31++G(d,p)		6-311++G(3df,2pd)		6-31G(d)		6-31++G(d,p)		6-311++G(3df,2pd)			
	Computed	Corrected	Computed	Corrected	Computed	Corrected	Computed	Corrected	Computed	Corrected	Computed	Corrected		
3062	3390	3064	3374	3062	3347	3063	3212	3108	3208	3135	3194	3123	A _{1g}	2
3053	3378	3053	3363	3052	3336	3053	3201	3098	3198	3126	3184	3113	E _{1u}	20b
3053	3378	3053	3363	3052	3336	3053	3201	3098	3198	3126	3184	3113	E _{1u}	20a
3048	3360	3036	3345	3036	3317	3036	3185	3083	3182	3110	3168	3098	E _{1g}	7b
3048	3360	3036	3345	3036	3317	3036	3185	3083	3182	3110	3168	3098	E _{1g}	7a
3048	3349	3026	3334	3025	3300	3020	3175	3073	3172	3101	3154	3084	B _{1u}	13
1599	1797	1625	1782	1617	1768	1618	1656	1603	1642	1605	1632	1596	E _{1g}	8b
1599	1797	1625	1782	1617	1768	1618	1656	1603	1642	1604	1632	1596	E _{1g}	8a
1482	1652	1493	1637	1486	1632	1493	1531	1482	1515	1481	1516	1482	E _{1u}	19b
1482	1652	1493	1637	1486	1632	1493	1531	1482	1515	1481	1515	1482	E _{1u}	19a
1350	1508	1363	1498	1360	1495	1368	1387	1342	1378	1347	1386	1355	A _{1g}	3
1309	1352	1222	1351	1226	1336	1222	1357	1313	1353	1322	1333	1304	B _{1u}	14
1178	1294	1170	1285	1166	1280	1172	1208	1169	1199	1172	1199	1173	E _{1g}	9b
1178	1294	1170	1284	1166	1280	1172	1208	1169	1198	1171	1199	1173	E _{1g}	9a
1146	1197	1082	1195	1084	1170	1071	1186	1147	1177	1150	1176	1150	B _{1u}	15
1037	1142	1032	1133	1028	1127	1032	1069	1035	1061	1037	1060	1037	E _{1u}	18b
1037	1142	1032	1133	1028	1127	1032	1069	1035	1061	1037	1060	1037	E _{1u}	18a
1010	1097	991	1096	994	974	892	1020	987	1018	995	933	912	B _{1u}	12
993	1084	980	1074	975	1070	979	1021	988	1013	990	1013	991	A _{1g}	1
990	1137	1027	1146	1040	1112	1018	1012	979	1010	987	996	974	B _{1g}	5
967	1100	995	1107	1004	1093	1000	970	939	985	963	988	966	E _{1u}	17b
967	1100	995	1107	1004	1093	1000	970	939	984	962	987	965	E _{1u}	17a
846	962	869	958	870	953	872	866	838	865	845	868	848	E _{1g}	10b
846	962	869	958	870	953	872	866	838	863	843	865	846	E _{1g}	10a
707	777	702	785	713	744	680	718	695	710	694	688	673	B _{1g}	4
673	765	691	759	688	757	692	696	673	689	673	690	675	A _{1u}	11
606	666	601	663	602	657	601	622	602	619	605	620	606	E _{1g}	6b
606	666	601	663	602	657	601	622	602	619	605	620	606	E _{1g}	6a
398	453	410	452	410	447	409	416	402	412	403	411	402	E _{1u}	16b
398	453	410	452	410	447	409	416	402	411	402	411	401	E _{1u}	16a

Kassae, M.H., Keffer, D.J., Steele, W.V., J. Molecular Structure: THEOCHEM, 800(1-3) 2007 p. 23-34.

Quantum Mechanics Still Requires Experiment

The state of the art of quantum mechanical calculations today is such that one requires an empirical scaling factor to correct vibrational frequencies computed from first principles. Tables of the frequencies have been generated as a function of basis set and method. They are averaged over many compounds.

Methods with standard basis sets

		STO-3G	3-21G	3-21G*	6-31G	6-31G*	6-31G**	6-31+G**	6-311G*	6-311G**	6-31G(2df,p)	cc-pVDZ	cc-pVTZ
hartree fock	HF	0.8165	0.9056	0.9026	0.9029	0.8985	0.9026	0.9042	0.9044	0.9085	0.9055	0.9080	0.9101
	ROHF	1.0000	0.9070	0.9085	0.8953	0.9025	0.8546	0.8559	0.8556	1.0000	1.0000	0.8607	0.8562
density functional	BLYP	0.9252	0.9945	0.9935	0.9924	0.9919	0.9923	0.9947	0.9975	0.9961	0.9945	1.0016	0.9970
	B3LYP	0.8924	0.9649	0.9620	0.9620	0.9603	0.9608	0.9642	0.9663	0.9668	0.9650	0.9700	0.9651
	B3LYPultrafine	1.0000	1.0000	1.0000	1.0000	0.9580	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
	B3PW91	0.8850	0.9612	0.9594	0.9577	0.9567	0.9584	0.9601	0.9627	0.9631	0.9614	0.9650	0.9616
	mPW1PW91	0.8789	0.9546	0.9465	0.9447	0.9483	0.9515	0.9518	0.9544	0.9567	0.9547	0.9583	0.9592
	PBEPBE	0.9136	0.9909	0.9555	0.9862	0.9857	0.9863	0.9886	0.9896	0.9909	0.9897	0.9942	0.9931
Moller Plesset perturbation	MP2FC	0.8719	0.9545	0.9513	0.9568	0.9430	0.9365	0.9406	0.9503	0.9502	0.9445	0.9525	0.9495
	MP2FU	1.0000	0.9548	0.9480	0.9501	0.9422	0.9344	0.9392	0.9471	0.9486	1.0000	0.9504	0.9361
	PMP2	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
	MP4	1.0000	0.9698	0.9438	0.9438	0.9548	0.9438	0.9438	0.9590	1.0000	1.0000	0.9438	0.9438
Configuration interaction	CID	1.0000	0.9316	0.9305	0.9352	0.9237	0.9240	0.9240	0.9291	1.0000	1.0000	0.9240	0.9265
	CISD	1.0000	0.9390	0.9344	0.9378	0.9258	0.9176	0.9218	0.9253	1.0000	1.0000	0.9218	0.9298
Quadratic configuration interaction	QCISD	1.0000	0.9692	0.9611	0.9636	0.9523	0.9414	0.9454	0.9574	0.9541	1.0000	0.9594	0.9537
	QCISD(T)	1.0000	0.9537	0.9537	0.9537	0.9593	0.9373	0.9390	0.9628	1.0000	1.0000	0.9531	0.9486
Coupled Cluster	CCD	1.0000	0.9723	0.9565	0.9595	0.9465	0.9376	0.9423	0.9551	1.0000	1.0000	0.9567	0.9337
	CCSD	1.0000	0.9431	0.9431	0.9431	0.9443	0.9326	0.9338	0.9535	1.0000	1.0000	0.9473	0.9412
	CCSD(T)	1.0000	0.9431	0.9431	0.9431	0.9621	0.9485	0.9596	0.9626	1.0000	1.0000	0.9788	0.9748

Thermodynamic Properties

Quantum Mechanics can be combined with Statistical Mechanics to provide thermodynamic properties like internal energy, enthalpy, entropy and free energy.

One requires a statistical mechanical model that provides a theoretical framework for expressing thermodynamic properties such as the entropy in terms of molecular level properties, such as the molecular symmetry number, the moment of inertia, the spectrum of normal frequencies, activation barriers to rotation, etc. One must understand that this mapping from QM to SM is in essence a coarse-graining procedure that reduces the number of degrees of freedom in the system. Like any other coarse-graining procedure, the mapping is approximate.

In large part, the most difficult thermodynamic property to determine experimentally or via computation is the entropy. For a polyatomic ideal gas in its ground electronic and nuclear states, the statistical mechanical model splits the entropy into four terms.

$$S_{total} = S_{translational} + S_{rotational} + S_{vibrational} + S_{internal\ rotational}$$

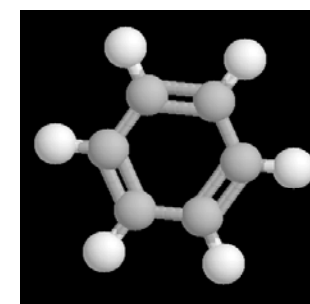
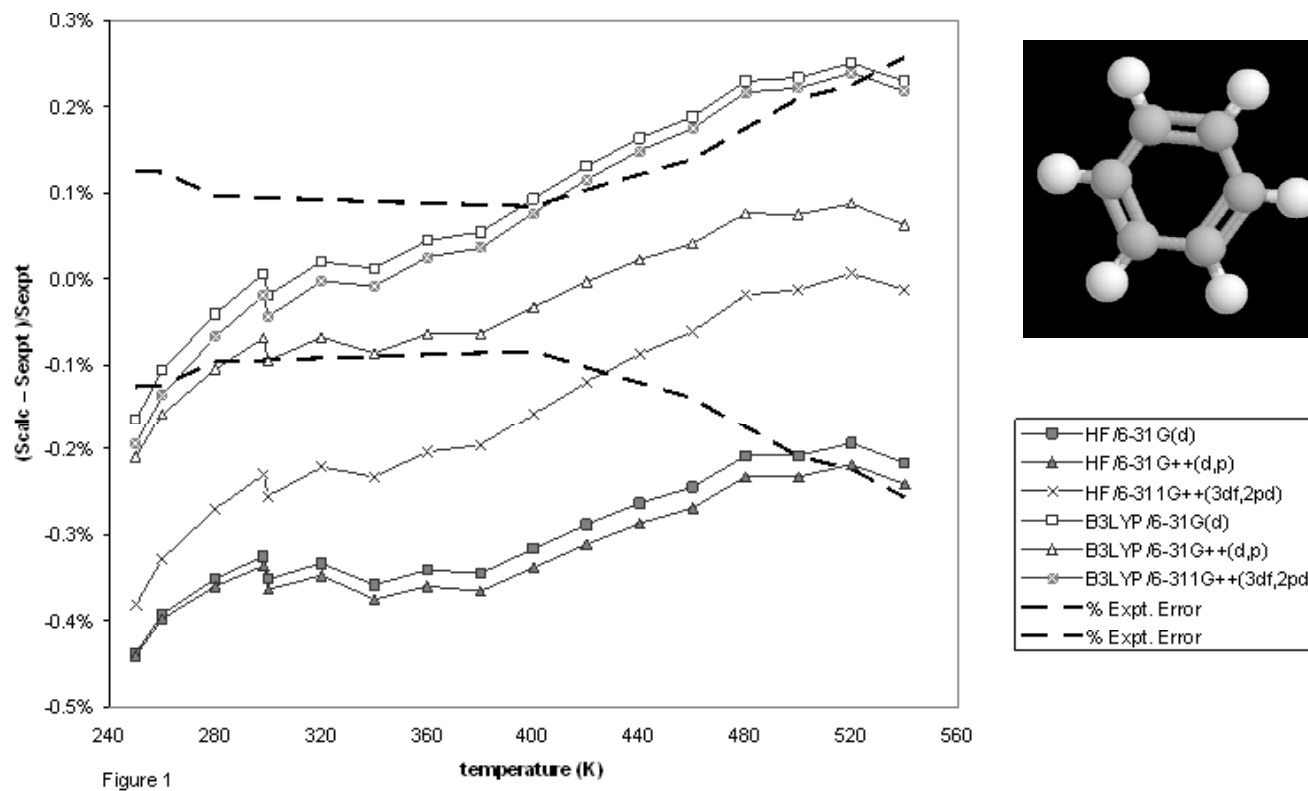
Thermodynamic Properties

The complete set of inputs for a statistical mechanical model used in the determination of these thermodynamic properties is given below. The properties in red come from QM calculations.

- molecular weight (for translation)
- **molecular moments of inertia (for rotation)**
- **symmetry number of molecule (for rotation)**
- number of vibrational modes (for vibration)
- **spectra of normal frequencies (for vibration)**
- number of internal rotors (for internal rotation)
- **rotor moments of inertia (for internal rotation)**
- **rotor activation energies (for internal rotation)**
- **enthalpy of formation (for energy reference)**
- molecular formula (for energy reference)
- reference temperature (for energy reference)

Thermodynamic Properties: Benzene

Here we show a comparison between experimental and calculated entropies as a function of both method and basis set for benzene.



Source: Kassae, M.H., Keffer, D.J., Steele, W.V., J. Molecular Structure: THEOCHEM, 800(1-3) 2007 p. 23-34.

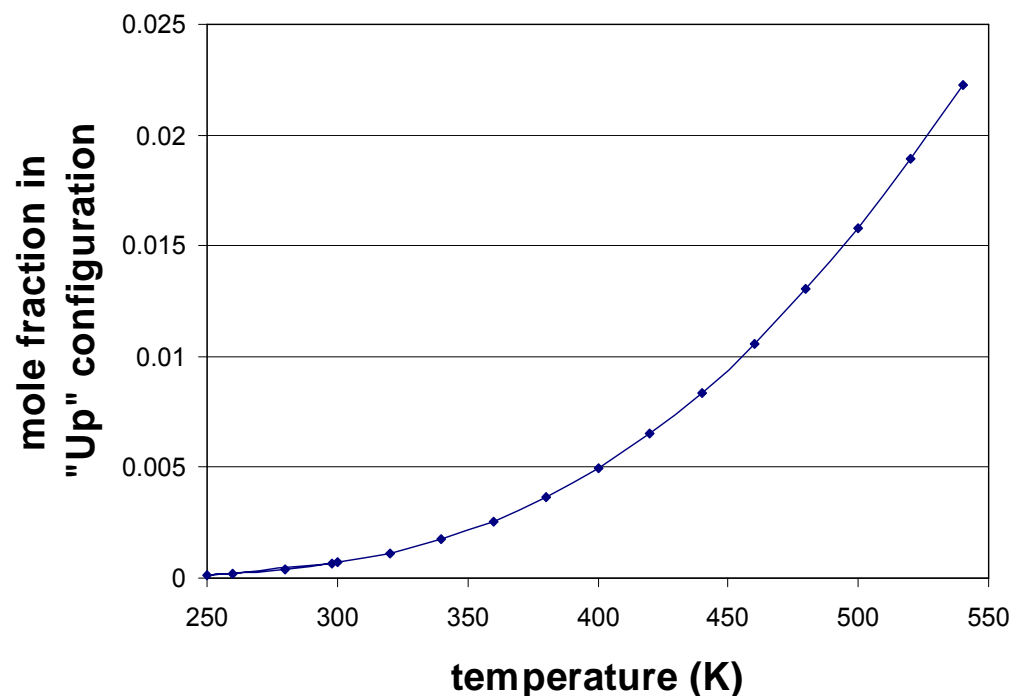
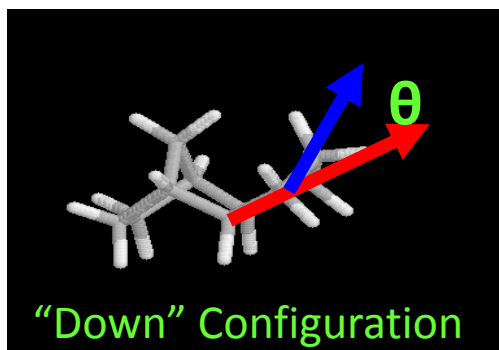
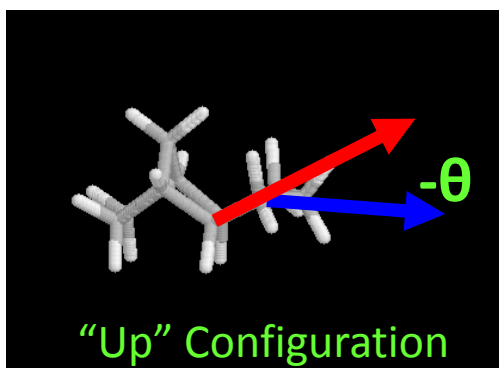
For a molecule that has two isomers or conformers, the ratio of the number of isomers of type one to the number of isomers of type two is related to the Gibbs free energy.

$$\begin{aligned}\frac{N_1}{N_2} &= \exp\left(-\frac{\Delta G_{1-2}}{RT}\right) = \exp\left(-\frac{\Delta H_{1-2} - T\Delta S_{1-2}}{RT}\right) \\ &= \exp\left(\frac{\Delta S_{1-2}}{R}\right) \exp\left(-\frac{\Delta H_{1-2}}{RT}\right)\end{aligned}$$

One can generate the enthalpy, H , and entropy, S , of each isomer and use it to compute the relative abundance of each isomer at thermodynamic equilibrium.

Thermodynamic Properties: JP-10

This procedure has been used to compute the relative configuration of the “up” and “down” configurations of the jet fuel, JP-10, as a function of temperature. The Gibbs free energy is calculated at each temperature for each compound. Based on the free energy difference, the relative distribution of configurations is readily determined. In this case, the “down configuration is much more stable and is predominant at low temperatures.



Thermodynamic Properties: dimethylnaphthalene



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There are 10 dimethylnaphthalene isomers. In order to compute the dimethylnaphthalene equilibrium distribution, one requires free energies.

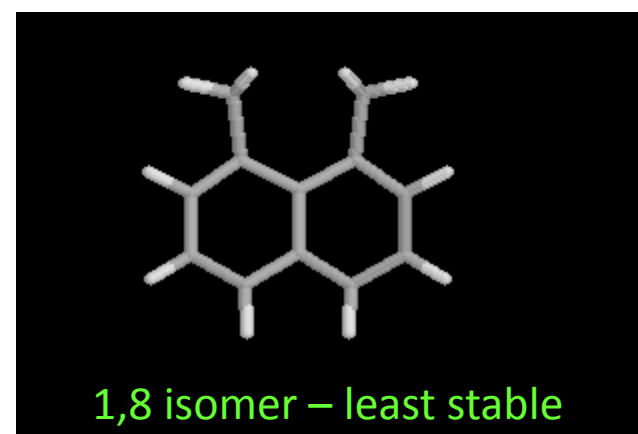
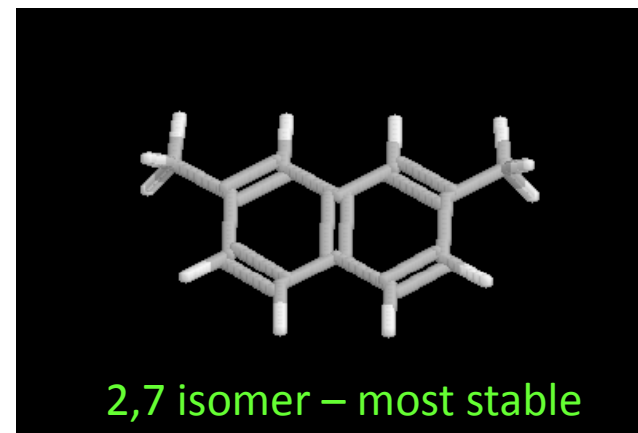
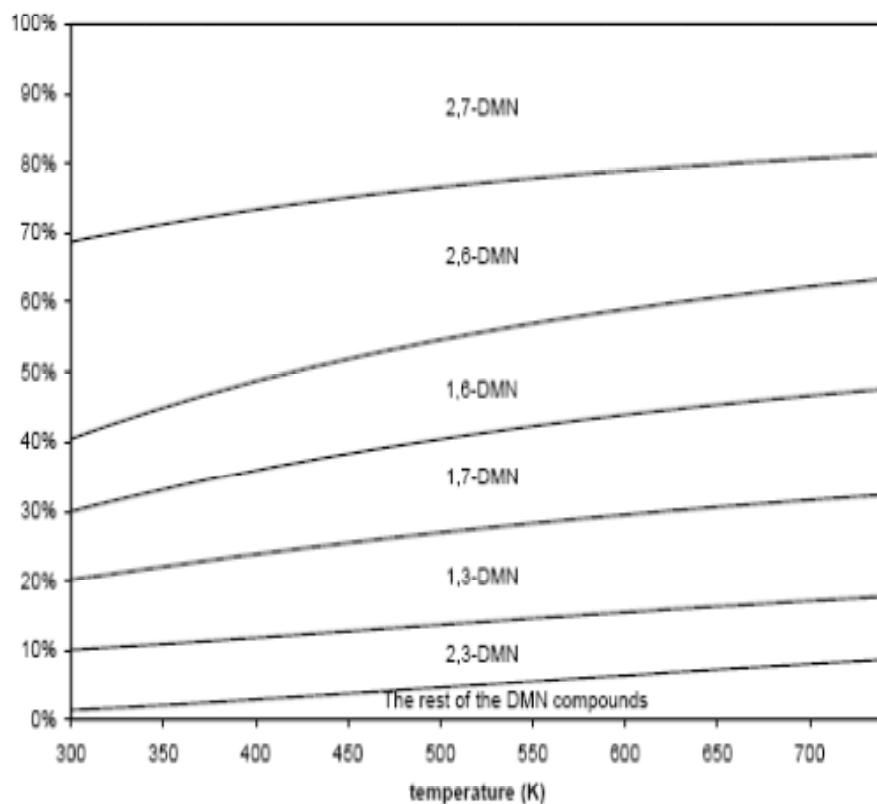
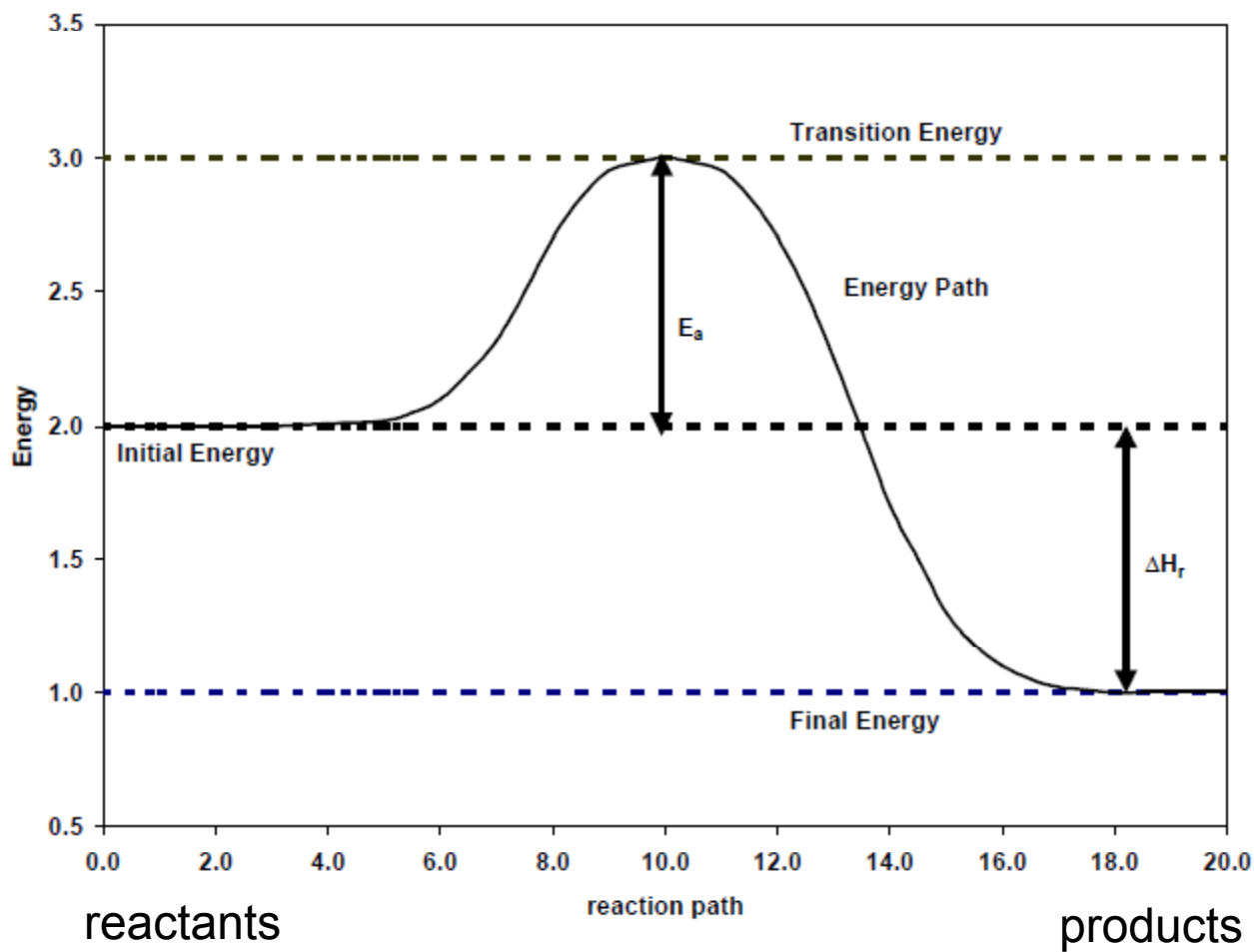


Figure 9 (a): Calculated equilibrium distribution of 2,3-DMN, 1,6-DMN, 1,3-DMN, 1,7-DMN, 2,7-DMN and 2,6-DMN and the sum distribution of the rest of the DMN compounds in the temperature range of 300-740 K with 20 K increments.

Kassae, M.H., Keffer, D.J., Steele, W.V., *J. Chem. Eng. Data*, **52**(5) 2007 p. 1843-1850.

Reaction Pathways and Kinetics

Quantum Mechanics can be combined with Transition State Theory to provide pathways for reactions and chemical kinetics.



statistical mechanics.¹⁹ According to transition-state theory, the rate constant of an elementary reaction can be estimated according to the following formula^{18,20}

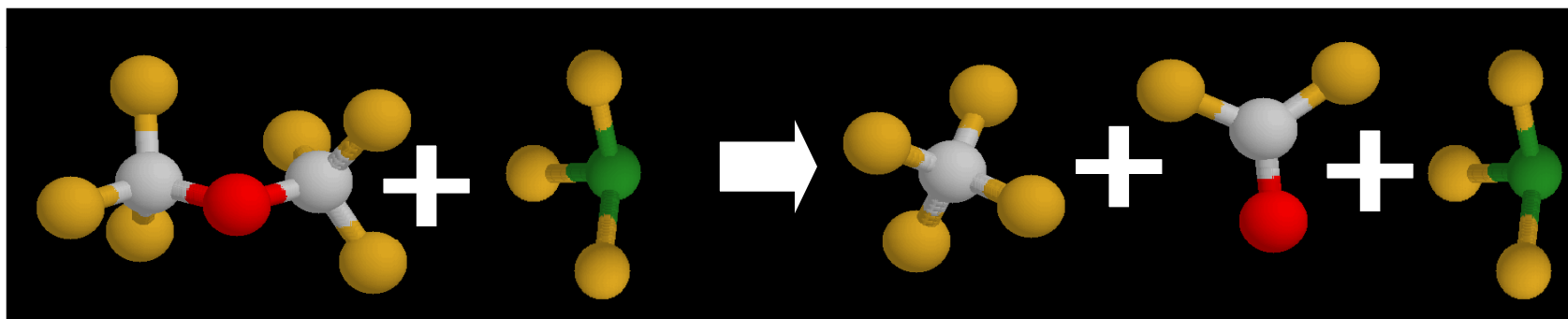
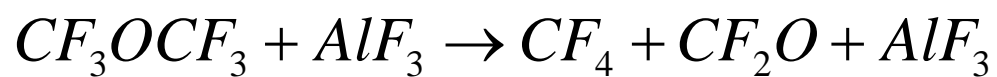
$$k = \kappa(T) \left(\frac{P_0}{RT_0} \right)^{-m} (k_B T/h) \exp(-\Delta G_0/RT) \quad (1)$$

where $\kappa(T)$ is the tunneling correction term, k_B is the Boltzmann constant, T_0 and P_0 are the temperature and pressure references, respectively, m is the change in the number of molecules from reactants to the transition state, h is Planck's constant, R is the ideal gas constant, T is the absolute temperature, and ΔG_0 is the change of the Gibbs free energy from reactants to the transition state. The Gibbs free energy change is expressed as

$$\kappa(T) = 1 + \frac{1}{24} \left(\frac{h\nu_s}{k_B T} \right)^2$$

Reaction Pathways and Kinetics

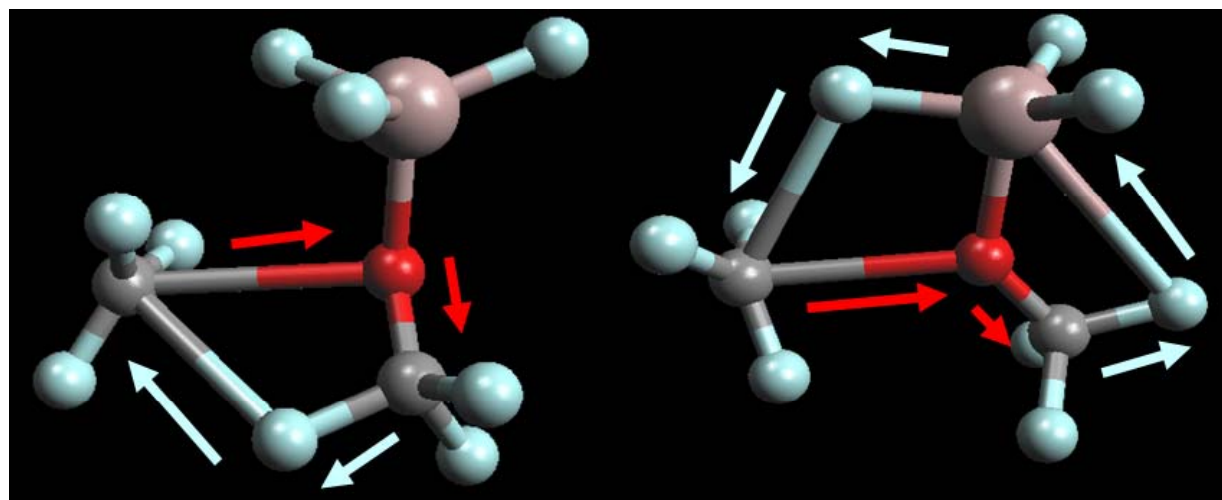
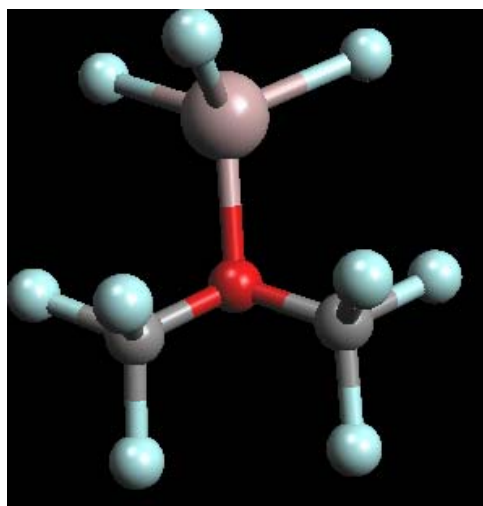
Example: catalytic decomposition of perfluorinated ethers



reactants

products

Reaction Pathways and Kinetics



old transition state

new transition state

red: O;
blue: F;
dark grey: C;
light grey: Al

Two fundamentally different transition structures identified
In TS₁, AlF₃ strictly stabilizes O
In TS₂, AlF₃ acts as a carrier of F from one C to another C

The new transition state lowers the activation energy from 228 to 199 kJ/mole, making the reaction 100,000 times faster at room temperature.

Jiang, B., Keffer, D.J., Edwards, B.J., J. Phys. Chem. A 112(12) 2008 pp. 2604-2609.

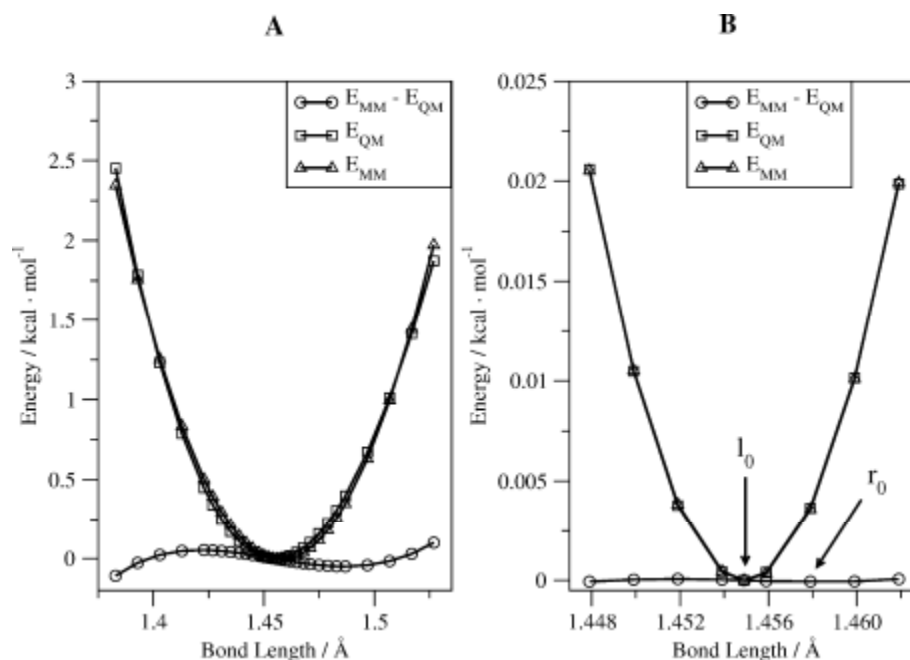
Parameterization of Classical Potentials

Quantum Mechanical calculations can provide data to parameterize classical potentials.

Example: Bond Stretching.

Quantum Mechanics: Solve Schrodinger eqn at many values of separation.

Classical Potential: Fit data to Hookean spring (parabola).



Quantum mechanical [MP2/6-31 + G(d,p)] and OPLS-AA/L stretching energy along the CR C(O) bond. The molecular mechanics parameters were fitted from two different intervals (from 1.38 to 1.52 Å (A) and from 1.448 to 1.462 Å (B) around the quantum mechanics equilibrium value. l_0 , QM minimum; r_0 , OPLS-AA/L reference bond length.

István Komáromi, Michael C. Owen, Richard F. Murphy, Sándor Lovas, Journal of Comp. Chem. 2008.

Capabilities of Quantum Mechanical Calculationsz

- I. What are Quantum Mechanical Calculations?
- II. Applications
 - II.A. Optimized Molecular Structures
 - II.B. Electronic Structure
 - II.C. Thermodynamic Properties
 - II.D. Reaction Pathways and Kinetics
 - II.E. Parameterization of Classical Potentials
- III. Strengths and Weaknesses
 - III.A. Theoretical Limitations
 - III.B. Computational Limitations
- IV. References

Strengths & Weaknesses



Quantum Mechanical calculations provide the means for computing electron distributions.

Limitations

Quantum Mechanical calculations are not exact.

Results vary from one choice of method and basis set to the next.

It is not always clear which method and basis set to use.

QM calculations still require empirical fudge factors for some properties, such as vibrational frequencies.

There are many problems for which QM calculations are known to perform poorly, such as the description of atoms with electrons in the f shell.

QM calculations are computationally expensive and scale poorly with the number of electrons.

References



- NIST Chemistry WebBook, <http://webbook.nist.gov/chemistry/>
- Jensen, F., “Introduction to Computational Chemistry”, Second Ed., Wiley & Sons, New York, 1999.
- Foresman, J.B., Frisch, Aeleen, “Exploring Chemistry with Electronic Structure Methods”, Second Ed., Gaussian Inc., Pittsburgh PA, 1996.