TEXAS A&M HIGH PERFORMANCE RESEARCH COMPUTING

Introduction to Quantum Mechanics Short Course

Lecture 4 of 6

TEXAS A&M UNIVERSITY
Division of Research

Density Functional Theory

- Functional – A function whose argument is also a function is called a functional.
- 1964 Hohenberg-Kohn Theorem (Kohn (DFT) split the Nobel prize with Pople (QM Methods) in 1998)
  - For $E_o(\rho)$, where ρ is the electron density of the ground state then ρ determines the number of electrons and the potential (ρ). Therefore, it also describes the ground state properties.

Density Functional Theory

- In theory, DFT is:
  - *ab initio*
  - variational
  - size-extensive
- The exact functional form is not known, therefore, an approximate functional that has been parameterized to fit experimental data is used. The functionals used today for DFT calculations are approximate and parameterized.
- Currently implemented DFT is:
  - not strictly *ab initio*
  - not variational
  - size-extensive

Density Functional Theory

$$E_{DFT}\left[\rho(r)\right]=T\left[\rho(r)\right]+V_{ne}\left[\rho(r)\right]+V_{ee}\left[\rho(r)\right]+\Delta T\left[\rho(r)\right]+\Delta V_{ee}\left[\rho(r)\right]$$

$T\left[\rho(r)\right]=$ Kinetic Energy of the non-interacting electrons

$V_{ne}\left[\rho(r)\right]=$ nuclei-electron coulombic attraction

$V_{ee}\left[\rho(r)\right]=$ electron-electron coulombic repulsion

$\Delta T\left[\rho(r)\right]=$ correction to the Kinetic Energy due to the interacting nature of all electrons

$\Delta V_{ee}\left[\rho(r)\right]=$ all non-classical corrections to the electron-electron interactions

$$E_{DFT}\left[\rho(r)\right]=$$

$$\sum_{i}^{N}\left(\langle\chi_i|-\frac{1}{2}\nabla^2|\chi_i\rangle-\langle\chi_i|\sum_{k}^{A}\frac{Z_A}{|r_i-r_k|}|\chi_i\rangle+\langle\chi_i|\frac{1}{2}\int\frac{\rho(r')}{|r_i-r'|}dr'|\chi_i\rangle\right)+E_{xc}\left[\rho(r)\right]$$

$$E_{xc}=\Delta T\left[\rho(r)\right]+\Delta V_{ee}\left[\rho(r)\right]$$

note : E_{xc} is commonly called the exchange-correlation energy, but remember that it contains a correction to the non-interacting electron kinetic energy term.

Density Functional Theory

$h_i^{ks}\chi_i = \varepsilon_i^{ks}\chi_i$

$$h_i^{ks} = -\frac{1}{2}\nabla_i^2 - \sum_k^A \frac{Z_k}{|r_i - r_k|} + \int \frac{\rho(r')}{|r_i - r'|}dr' + V_{xc}$$

$$V_{xc} = \frac{\partial E_{xc}}{\partial \rho}$$

$H_{ks}C = SC\varepsilon_{ks}$

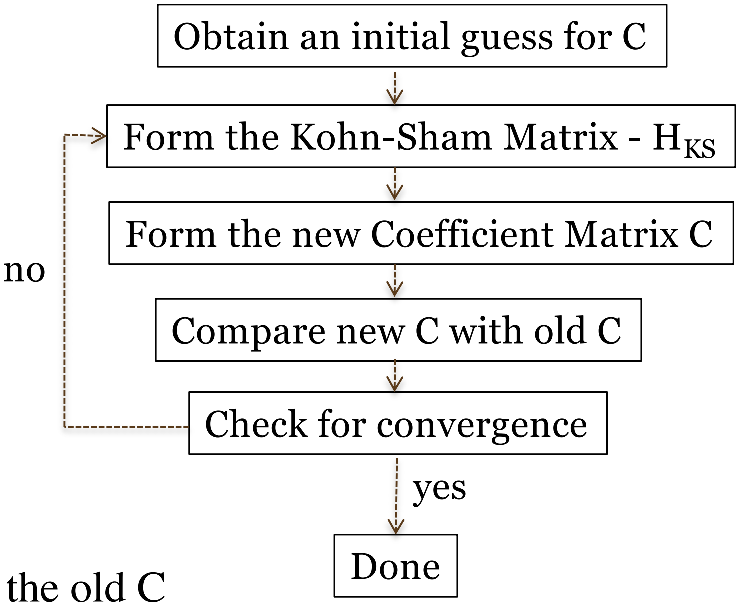
$H_{ks}C = SC\varepsilon_{ks}$ is solved iteratively:

$H_{KS}C = SC\varepsilon_{ks}$ is transformed to $H'_{ks}C' = C'\varepsilon_{ks}$

H'_{ks} is then diagonalized to so solve for ε_{ks}

C' is transformed back to C and compared with the old C

The procedure continues until convergence is reached



Density Functional Theory

$\langle \chi_i | V_{xc} | \chi_j \rangle$ cannot be solved analytically.

Therefore, numerical methods must be used:

$$\langle \chi_i | V_{xc} | \chi_j \rangle \cong \sum_{k}^{G} V_{xc}\left(\rho(r_k)\nabla\rho(r_k)\nabla^2\rho(r_k)\chi_i(r_k)\chi_j(r_k)\right)\nabla V_k$$

where, G is the number of grid points

The grid is normally spherical around the nucleus.

In Gaussian 09, (75,302) is defined as:

75 shells with 302 points on each shell.

A pruned grid decreases the number of points near the nucleus.

Optimization of Large "Floppy" Molecules

- From the G09 manual:
    - int=(UltraFine) requests a pruned (99,590) grid. It is recommended for molecules containing lots of tetrahedral centers and for computing very low frequency modes of systems. This grid is also useful for optimizations of **larger** molecules with many **soft modes such as methyl rotations**, making such optimizations more reliable.
- In G16 the UltraFine grid is default
- You have to use the same grid for all calculation that you are using to obtain relative energies (ie ΔG_{rxn})

Implementations of DFT

- Local Density Approximation
- Gradient Corrected or Generalized Gradient Approximation (GGA)
- Meta-Generalized Gradient Approximation
- Hybrid Methods that include exact HF exchange
- Long Range and Dispersion Corrected Functionals
- Double-Hybrid DFT
- Include Unoccupied KS orbitals (MR-DFT)

Density Functional Theory

- Local Density Approximation - $E_{DFT}(\rho(r))$

exchange :

$$\text{Slater} \quad \rho^{\frac{4}{3}}\left(\frac{2}{3}\right)$$

$$\text{LSDA and } X_{\alpha} \quad \rho^{\frac{4}{3}}(0.75)$$

correlation :

VWN (Vosko, Wilk,and Nusair)

VWN is designed to reproduce the correlation energy of a uniform electron gas.

VWN (functional III)

$$\varepsilon_c^{\mathrm{VWN}}(r_S,\zeta)=\varepsilon_c(r_S,0)+\varepsilon_a(r_S)\left[\frac{f(\zeta)}{f''(0)}\right][1-\zeta^4]+[\varepsilon_c(r_S,1)-\varepsilon_c(r_S,0)]f(\zeta)\zeta^4$$

$$f(\zeta)=\frac{(1+\zeta)^{4/3}+(1-\zeta)^{4/3}-2}{2(2^{1/3}-1)}$$

$$\varepsilon_{c/a}(x)=A\left\{\begin{array}{c}\ln\frac{x^2}{X(x)}+\frac{2b}{Q}\tan^{-1}\left(\frac{Q}{2x+b}\right)-\\ \frac{bx_0}{X(x_0)}\left[\ln\frac{(x-x_0)^2}{X(x)}+\frac{2(b+2x_0)}{Q}\tan^{-1}\left(\frac{Q}{2x+b}\right)\right]\end{array}\right\}$$

$$x=\sqrt{r_S}$$

$$X(x)=x^2+bx+c$$

$$Q=\sqrt{4c-b^2}$$

$$\zeta=\frac{\rho^\alpha-\rho^\beta}{\rho^\alpha+\rho^\beta},\quad \frac{4}{3}\pi r_S^3=\rho^{-1}$$

The parameters A, x_0, b and c are fitting constants, different for $\varepsilon_c(r_S,0)$, $\varepsilon_c(r_S,1)$, and $\varepsilon_a(r_S)$.

Density Functional Theory

- Gradient Corrected or Generalized Gradient Approximation (GGA) - $E_{DFT}(\rho(r),\nabla\rho(r))$
- Exchange:
  - B (Becke)

$$\varepsilon_x^{B} = \varepsilon_x^{LDA} + \Delta\varepsilon_x^{B88} \quad ; \quad \Delta\varepsilon_x^{B88} = -\beta\rho^{\frac{1}{3}}\frac{x^2}{1+6\beta x\sinh^{-1}x} \quad ; \quad x = \frac{|\nabla\rho|}{\rho^{\frac{4}{3}}}$$

  - PW91 (Perdew and Wang)

$$\varepsilon_{\mathrm{x}}^{\mathrm{PW91}} = \varepsilon_{\mathrm{x}}^{\mathrm{LDA}}\left(\frac{1+xa_1\sinh^{-1}(xa_2)+(a_3+a_4e^{-bx^2})x^2}{1+xa_1\sinh^{-1}(xa_2)+a_5x^2}\right)$$

Density Functional Theory

- Correlation:
  - LYP (Lee, Yang, and Parr)
    - a, b, c, and d parameters are determined by
    - fitting to data for the helium atom

$$\varepsilon_c^{\text{LYP}} = -a\frac{\gamma}{(1+d\rho^{-1/3})} - ab\frac{\gamma e^{-c\rho^{-1/3}}}{9(1+d\rho^{-1/3})\rho^{8/3}} \times \left[\begin{array}{l} 18(2^{2/3})C_F(\rho_\alpha^{8/3}+\rho_\beta^{8/3}) - 18\rho t_W \\ +\rho_\alpha(2t_W^\alpha + \nabla^2\rho_\alpha) + \rho_\beta(2t_W^\beta + \nabla^2\rho_\beta) \end{array}\right]$$

$$\gamma = 2\left[1 - \frac{\rho_\alpha^2 + \rho_\beta^2}{\rho^2}\right]$$

$$t_W^\sigma = \frac{1}{8}\left(\frac{|\nabla\rho_\sigma|^2}{\rho_\sigma} - \nabla^2\rho_\sigma\right)$$

  - P86 (Perdew)

$$\varepsilon_c^{\text{P86}} = \varepsilon_c^{\text{LDA}} + \Delta\varepsilon_c^{\text{P86}}$$

$$\Delta\varepsilon_c^{\text{P86}} = \frac{e^{\Phi}C(\rho)|\nabla\rho|^2}{f(\zeta)\rho^{7/3}}$$

$$f(\zeta) = 2^{1/3}\sqrt{\left(\frac{1+\zeta}{2}\right)^{5/3} + \left(\frac{1-\zeta}{2}\right)^{5/3}}$$

$$\Phi = a\frac{C(\infty)|\nabla\rho|}{C(\rho)\rho^{7/6}}$$

$$C(\rho) = \mathscr{C}_1 + \frac{\mathscr{C}_2 + \mathscr{C}_3 r_S + \mathscr{C}_4 r_S^2}{1 + \mathscr{C}_5 r_S + \mathscr{C}_6 r_S^2 + \mathscr{C}_7 r_S^3}$$

  - PW91 (Perdew and Wang)

$$\varepsilon_{c/a}^{\text{PW91}}(x) = -2a\rho(1+\alpha x^2)\ln\left(1 + \frac{1}{2a(\beta_1 x + \beta_2 x^2 + \beta_3 x^3 + \beta_4 x^3)}\right)$$

Here a, α, β_1, β_2, β_3 and β_4 are suitable constants.

Density Functional Theory

- Gradient Corrected or Generalized Gradient Approximation (GGA) - $E_{DFT}(\rho(r),\nabla\rho(r))$
- Exchange:
  - B (Becke)
  - PW91 (Perdew and Wang)
- Correlation:
  - LYP (Lee, Yang, and Parr)
  - P86 (Perdew)
  - PW91 (Perdew and Wang)
- Exchange-Correlation together:
  - BLYP, BP86, PW91PW91, etc

Density Functional Theory

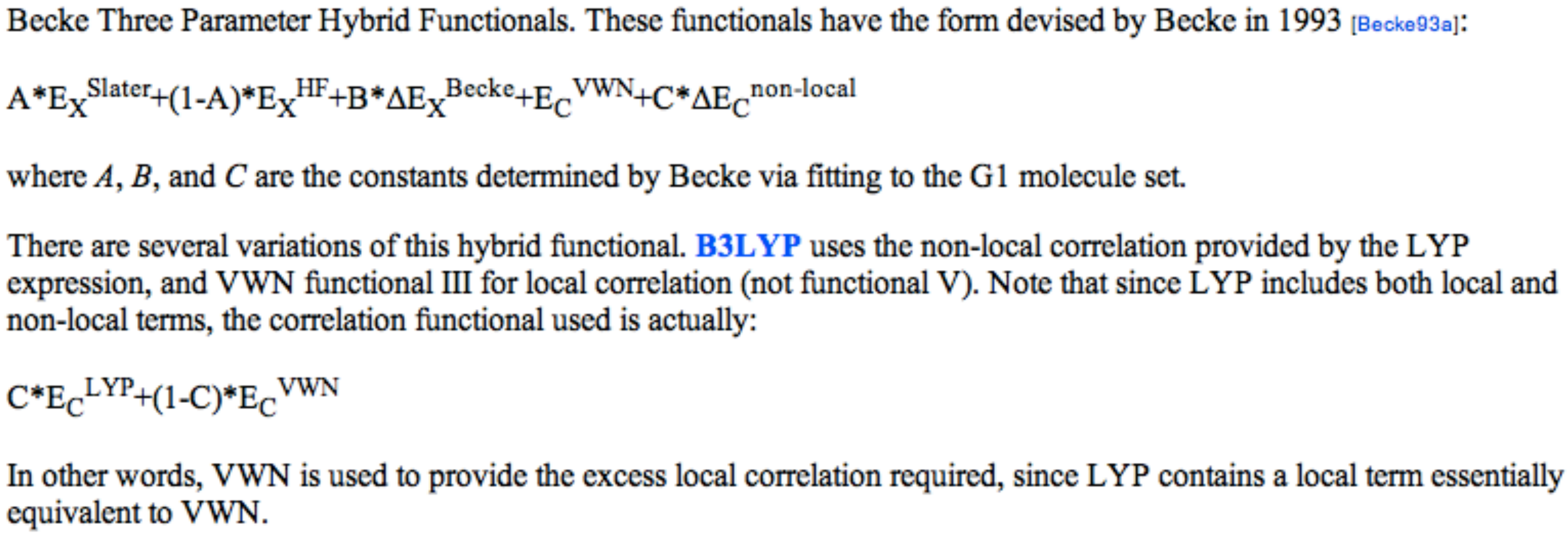
- Meta-Generalized Gradient Approximation (τ-GGA) - $E_{DFT}(\rho(r),\nabla\rho(r),\nabla^2\rho(r))$
- Exchange:
  - TPSS (Tao and Perdew)
- Correlation:
  - TPSS (Tao and Perdew)
- Exchange and Correlation together
  - TPSSTPSS
- Standalone Exchange and Correlation
  - M06L (Truhlar)

Density Functional Theory

- Hybrid Methods that include exact HF exchange
- Exchange $E_{DFT}(\rho(r),\nabla\rho(r))$:
  - B3 (Becke)
- Standalone Exchange and Correlation $E_{DFT}(\rho(r),\nabla\rho(r),\nabla^2\rho(r))$:
  - M06 (Truhlar)
  - BMK (Boese and Martin)
  - TPSSh (Tao and Perdew)

B3LYP

- From the Gaussian on-line manual:



Becke Three Parameter Hybrid Functionals. These functionals have the form devised by Becke in 1993 [Becke93a]:

$A*E_X^{Slater}+(1-A)*E_X^{HF}+B*\Delta E_X^{Becke}+E_C^{VWN}+C*\Delta E_C^{non\text{-}local}$

where *A*, *B*, and *C* are the constants determined by Becke via fitting to the G1 molecule set.

There are several variations of this hybrid functional. **B3LYP** uses the non-local correlation provided by the LYP expression, and VWN functional III for local correlation (not functional V). Note that since LYP includes both local and non-local terms, the correlation functional used is actually:

$C*E_C^{LYP}+(1-C)*E_C^{VWN}$

In other words, VWN is used to provide the excess local correlation required, since LYP contains a local term essentially equivalent to VWN.

Long-range and/or dispersion corrected Functionals

- Long-range corrected functionals (some with dispersion)
  - LC-ωPBE
  - ωB97
  - ωB97X
    - includes HF exchange
  - ωB97XD
    - includes HF exchange and an empirical correction for dispersion
  - CAM-B3LYP
  - LC-*pure_functional*
- Dispersion corrected
  - EmpiricalDispersion=
    - PFD, GD2, GD3, GD3BJ,

(note: B97D and B97XD does not include the long range correction but included the empirical correction for dispersion)

CAM-B3LYP

A new hybrid exchange–correlation functional named CAM-B3LYP is proposed. It combines the hybrid qualities of B3LYP and the long-range correction presented by Tawada et al. [J. Chem. Phys., in press]. We demonstrate that CAM-B3LYP yields atomization energies of similar quality to those from B3LYP, while also performing well for charge transfer excitations in a dipeptide model, which B3LYP underestimates enormously. The CAM-B3LYP functional comprises of 0.19 Hartree–Fock (HF) plus 0.81 Becke 1988 (B88) exchange interaction at short-range, and 0.65 HF plus 0.35 B88 at long-range. The intermediate region is smoothly described through the standard error function with parameter 0.33.

http://dx.doi.org/10.1016/j.cplett.2004.06.011

CAM-B3LYP

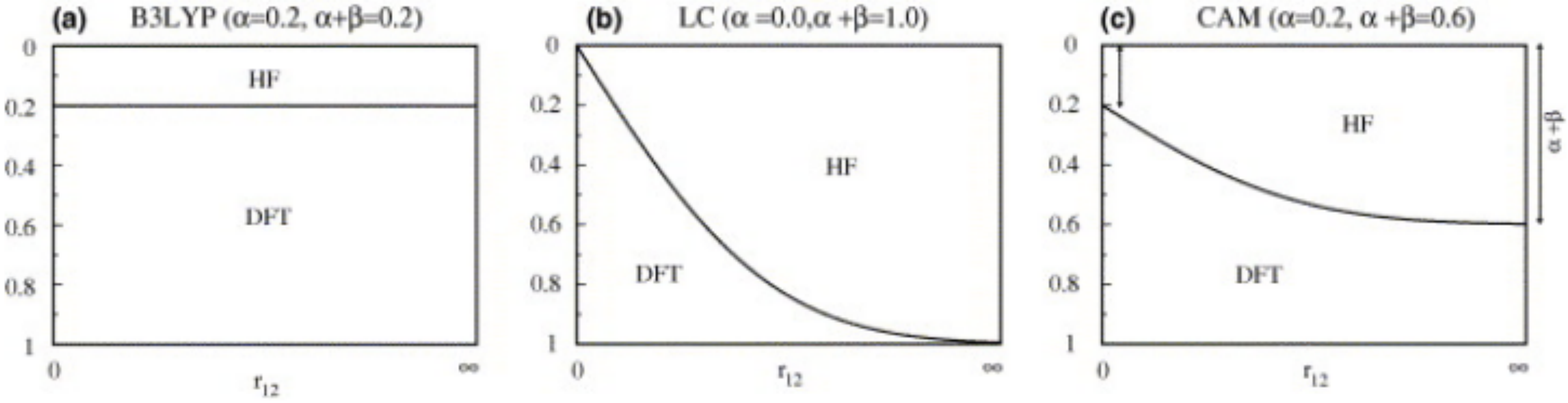


Fig. 2.

Schematic plots of the contributions to exchange from r_{12}^{-1}, apportioned into DFT and HF, for: (a) B3LYP, (b) LC, and (c) CAM.

http://dx.doi.org/10.1016/j.cplett.2004.06.011

Dispersion Correction

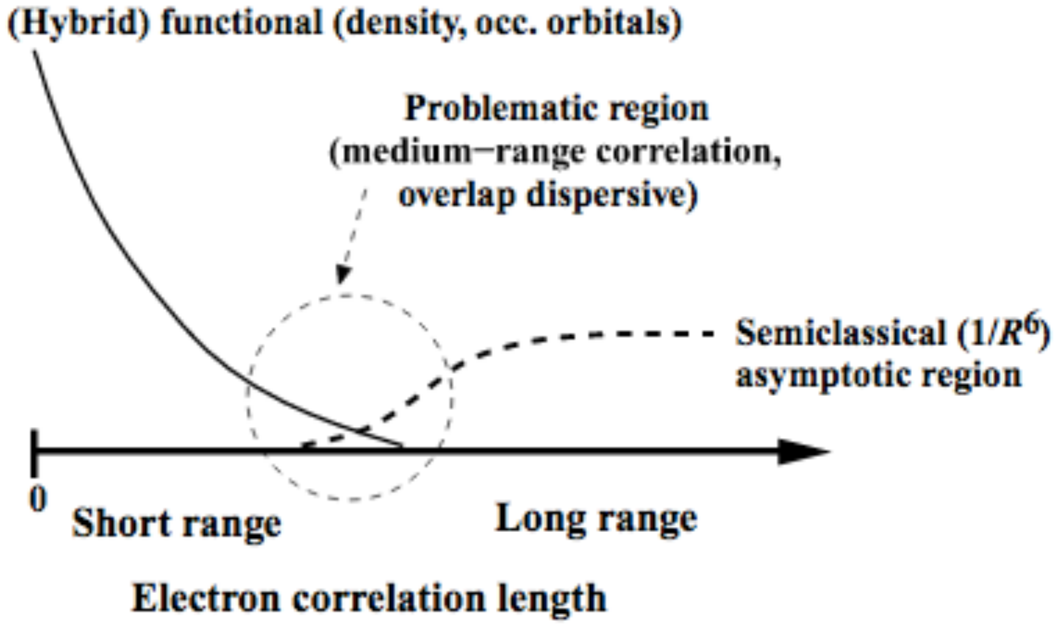
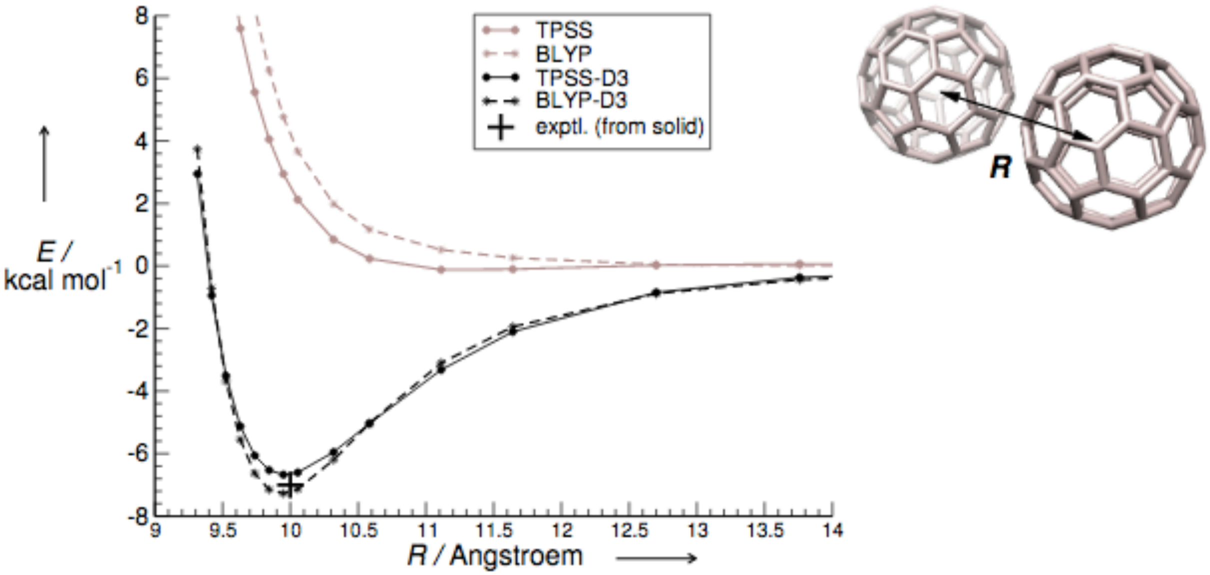


FIGURE 3 | Schematic classification of the correlation and dispersion problems on different electron correlation length scales.

http://onlinelibrary.wiley.com/doi/10.1002/wcms.30/pdf

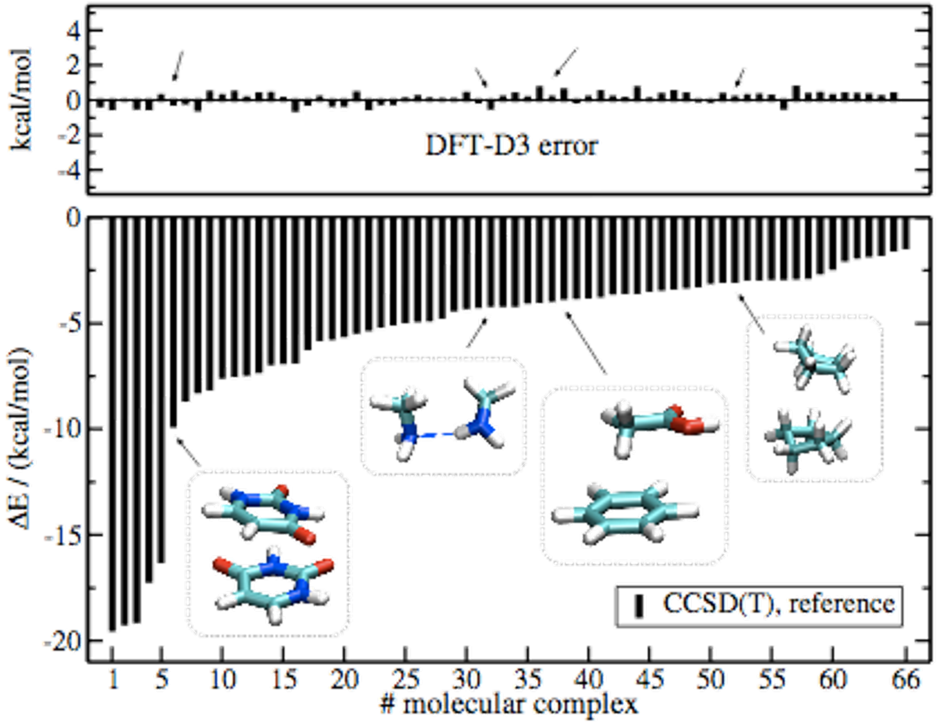
Dispersion Corrected

A large vdW complex as an example: the C_{60} dimer



Non-covalent interaction energies for small systems: typically <5% error with disp.-corr. DFT

S66 benchmark set (Hobza et al, JCTC, 7, 2011, 2427)



MAD

DFT-D3/NL:
0.2-0.5 kcal/mol

MP2/CBS:
0.45 kcal/mol

semi-emp.-D3:
0.7-1 kcal/mol

conventional DFs:
>1-3 kcal/mol

Functionals available in G16

- EXCHANGE FUNCTIONALS: Slater, Xα, Becke 88, Perdew-Wang 91, Barone-modified PW91, Gill 96, PBE, OPTX, TPSS, revised TPSS, BRx, PKZB, ωPBEh/HSE, PBEh
- CORRELATION FUNCTIONALS: VWN, VWN5, LYP, Perdew 81, Perdew 86, Perdew-Wang 91, PBE, B95, TPSS, revised TPSS, KCIS, BRC, PKZB, VP86, V5LYP
- OTHER PURE FUNCTIONALS: VSXC, HCTH functional family, τHCTH, B97D, M06L, SOGGA11, M11L, MN12L, N12, MN15L
- HYBRID METHODS: B3LYP, B3P86, P3PW91, B1 and variations, B98, B97-1, B97-2, PBE1PBE, HSEh1PBE and variations, O3LYP, TPSSh, τHCTHhyb, BMK, AFD, M05, M052X, M06, M06HF, M062X, M08HX, PW6B95, PW6B95D3, M11, SOGGA11X, N12, MN12SX, N12SX, MN15, HISSbPBE, X3LYP, BHandHLYP; user-configurable hybrid methods
- EMPIRICAL DISPERSION: PFD, GD2, GD3, GD3BJ
- FUNCTIONALS INCLUDING DISPERSION: APFD, B97D3, B2PLYPD3
- LONG RANGE-CORRECTED: LC-ωPBE, CAM-B3LYP, ωB97XD and variations, Hirao’s general LC correction

Double-Hybrid DFT

$$E_{XC} = (1 - a_X)\, E_X^{DFT} + a_X E_X^{HF} + (1 - a_C)\, E_C^{DFT} + a_C E_C^{PT2}$$

- Double-Hybrid DFT methods have the same computational cost as MP2
- Gaussian includes Grimme’s B2PLYP and mPW2PLYP methods(via keywords of the same name); the empirical dispersion corrected variations are specified by appending a D to the keyword name: e.g., B2PLYPD for B2PLYP with empirical dispersion. B2PLYPD3 requests the same but with Grimme's D3BJ dispersion.

Density Functional Theory – MR-DFT

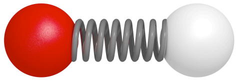
- Include unoccupied Kohn-Sham orbitals

Density Functional Theory

- Pros:
  - Include dynamic electron correlation for about the same computational cost as Hartree-Fock
  - Often is more robust for systems with multi-reference character – transition metals, etc
- Cons:
  - No Hierarchy
  - Poor for dispersion
  - Pure DFT tends to overbind

Molecular Mechanics

- The molecule is considered to be a collection of atoms held together by simple elastic or harmonic forces.



- Force Field - A mathematical expression that describes the dependence of the energy of a molecule on the coordinates of the atoms in the molecule.

- Force Field Energy Expression:

$$E = E_{bond} + E_{angle} + E_{torsion} + E_{oop} + E_{nonbond} + E_{other}$$

Molecular Mechanics

- The potential is approximated by an empirical function force field that is fitted to approximately reproduce known interactions
- Applicability is limited by the availability of parameterization
- Generally, the connectivity of atoms cannot change during the simulation
- Generally not suitable for reaction mechanisms
- Can predict relative energies of different conformational states of material
- And more

Class I Force Field Potential

Intramolecular (internal, bonded terms)

$$\sum_{bonds} K_b(b-b_o)^2 + \sum_{angles} K_\theta(\theta-\theta_o)^2 + \sum_{torsions} K\phi(1+\cos(n\phi-\delta))$$

$$+ \sum_{impropers} K_\varphi(\varphi-\varphi_o)^2 + \sum_{Urey-Bradley} K_{UB}(r_{1,3}-r_{1,3,o})^2$$

Intermolecular (external, nonbonded terms)

$$\sum_{nonbonded} \frac{q_i q_j}{4\pi D r_{ij}} + \varepsilon_{ij}\left[\left(\frac{R_{\min,ij}}{r_{ij}}\right)^{12} - 2\left(\frac{R_{\min,ij}}{r_{ij}}\right)^{6}\right]$$

Molecular Mechanics

- Force Fields differ in their parameters, cross terms and the method of development
  - Class I - simple functional form with data fitted to quantum mechanical calculations and/or experiment
  - Class II - more complicated functional form using cross terms and data fitted to quantum mechanical calculations and/or experiment
  - Class III - new generation force fields that incorporate polarizability
- Rules Based - covers most of the periodic table
  - Fundamental quantities are derived for each atom type: electronegativity, hardness, atomic radius, etc.
  - Forcefield parameters are derived at runtime using a series of theoretically or empirically derived rules
- Specialist - developed for a particular family of compounds flourinated polymers, zeolites, etc.

Common Force Fields

- MM2/3/4: Molecular Mechanic Force field for small molecules
- CHARMM: Chemistry at Harvard Macromolecular Mechanics
- AMBER: Assisted Model Building with Energy Refinement
- OPLS: Optimized Parameters for Liquid Simulation
- CFF: Consistent Force Field
- CVFF: Valence Consistent Force Field
- MMFF94: Merck Molecular Force Field 94
- DREIDING: Generic rules based force field
- UFF: Universal Force Field

UFF Force Field

- UFF has full coverage of the periodic table. UFF is moderately accurate for predicting geometries and conformational energy differences of organic molecules, main-group inorganics, and metal complexes. It is recommended for organometallic systems and other systems for which other forcefields do not have parameters.
- The Universal forcefield includes a *parameter generator* that calculates forcefield parameters by combining atomic parameters. Thus, forcefield parameters for any combination of atom types can be generated as required.
- Dummy atoms are used in π-complexation and are associated with explicit parameters.

UFF - Universal Force Field

- The Universal forcefield's atom types are denoted by an element name of one or two characters followed by up to three other characters:
  - The first two characters are the element symbol (i.e., N_ for nitrogen).
  - The third character (if present) represents the hybridization state
    - 1 = linear
    - 2 = trigonal
    - R = an atom involved in resonance
    - 3 = tetrahedral
    - 4 = square planar
    - 5 = trigonal bipyramidal
    - 6 = octahedral
  - The fourth and fifth characters (if present) indicate characteristics such as
    - the oxidation state (i.e., Rh6+3 represents octahedral Rh in the +3 formal oxidation state
    - H___b indicates a diborane bridging hydrogen type
    - O_3_z is a framework oxygen type suitable for zeolites).

UFF Force Field

Bond Stretch Term:

$$E_R = \frac{1}{2} k_{IJ} \left(r - r_{IJ} \right)^2 \qquad \text{Harmonic} \leftarrow$$

Default in Gaussian use iop(4/33=3) to have Gaussian print detailed information about the parameters used.

$$E_R = D_{IJ} \left[e^{-\alpha\left(r - r_{IJ} \right)} - 1 \right] ; \ \alpha = \left[\frac{k_{IJ}}{2D_{IJ}} \right]^{\frac{1}{2}} \qquad \text{Morse}$$

$$r_{IJ} = r_I + r_J + r_{BO} + r_{EN}$$

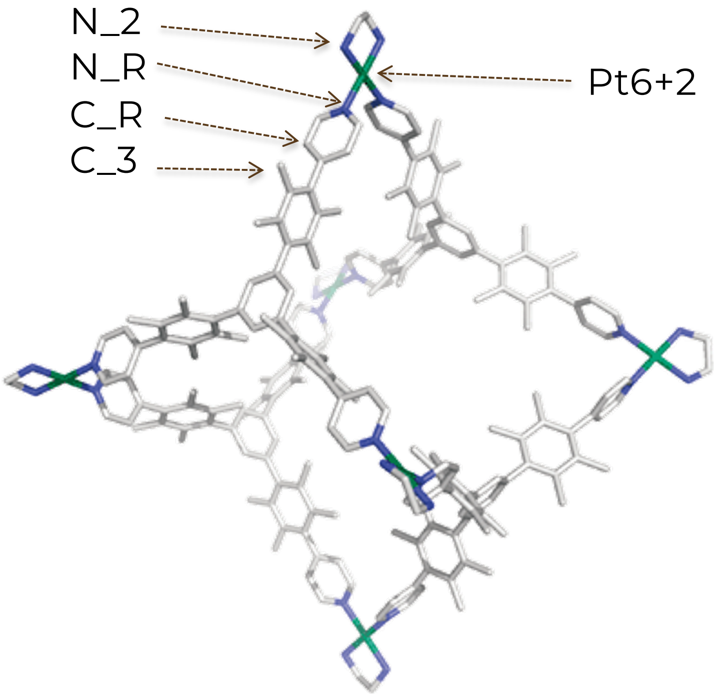
r_I = bond radii of atom I ; r_J = bond radii of atom J

$$r_{BO} = -\lambda \left(r_I + r_J \right) \ln(n) \, ; \, \lambda = 0.1332$$

$$r_{EN} = r_I r_J \frac{\left(\sqrt{\chi_I} - \sqrt{\chi_J} \right)^2}{\left(\chi_I r_I + \chi_J r_J \right)}$$

n – bond order tuning parameter

Atom Types



"Geometry optimized structure of the Pt(II)-linked cage by using Accelrys's program "Forcite" with force field "Universal" on Materials Studio 4.0. Hydrogen atoms are omitted for clarity."

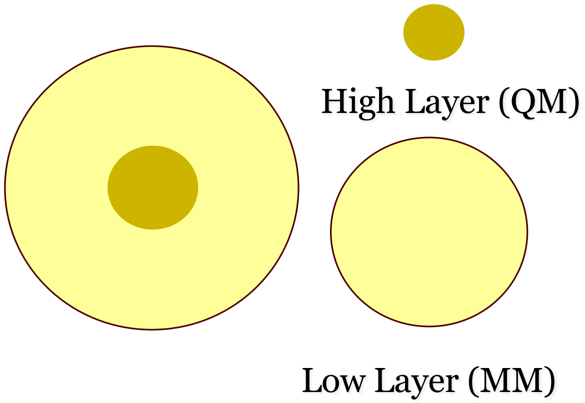
DOI: 10.1039/B817713A (Paper) New J. Chem., 2009, 33, 264-270

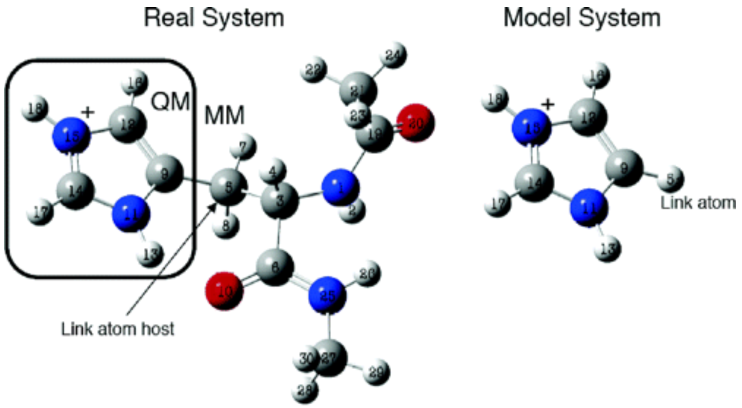
ONIOM

ONIOM (Our own N-layered Integrated molecular Orbital and molecular Mechanics)

$$E^{ONIOM(QM:MM)} = E^{QM}_{model} + E^{MM}_{real} - E^{MM}_{model}$$

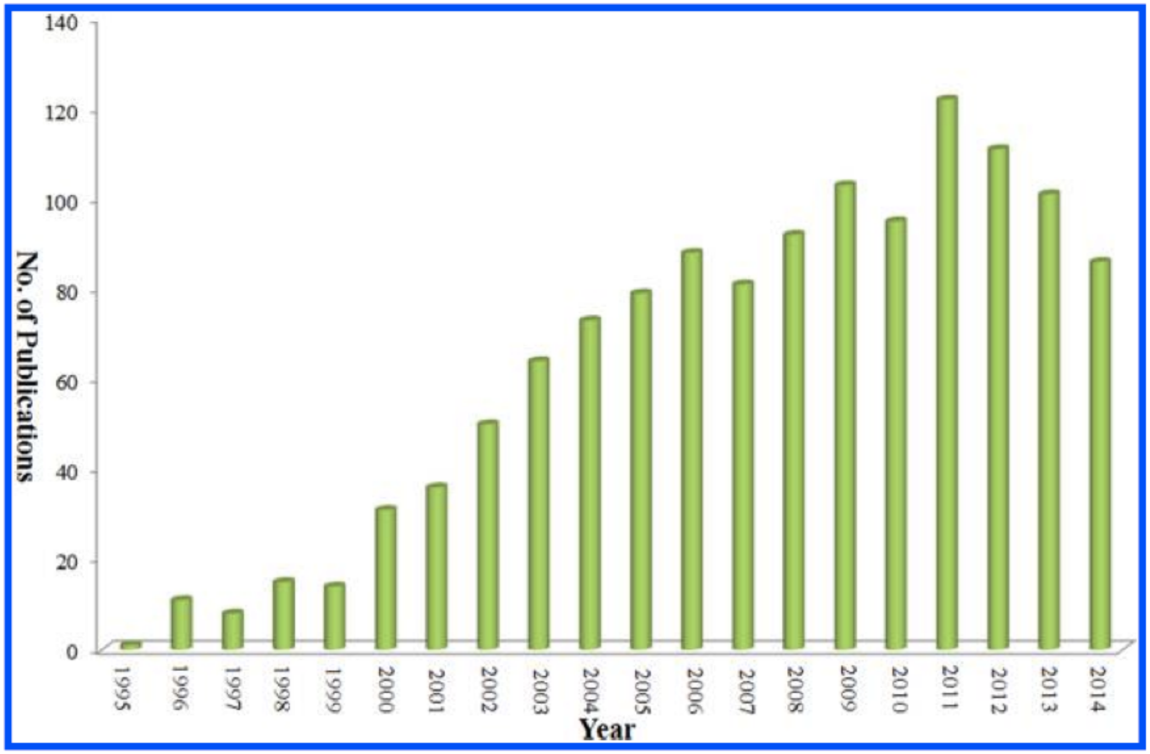
$$= E^{high}_{model} + E^{low}_{real} - E^{low}_{model}$$



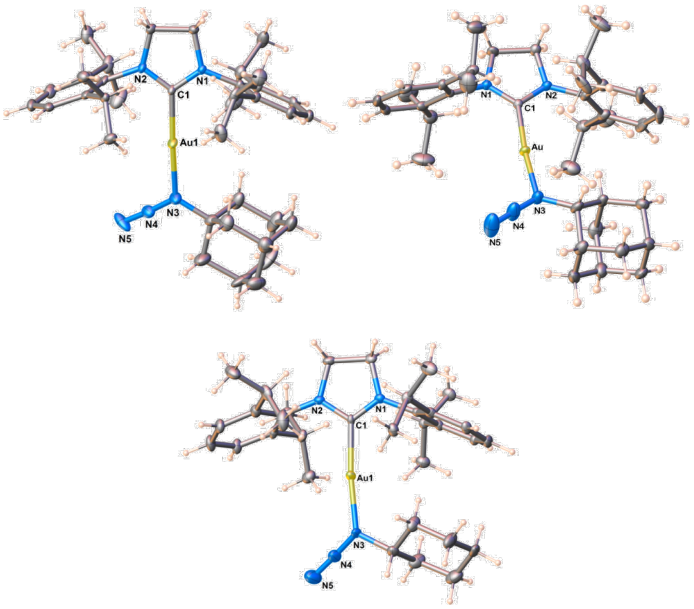


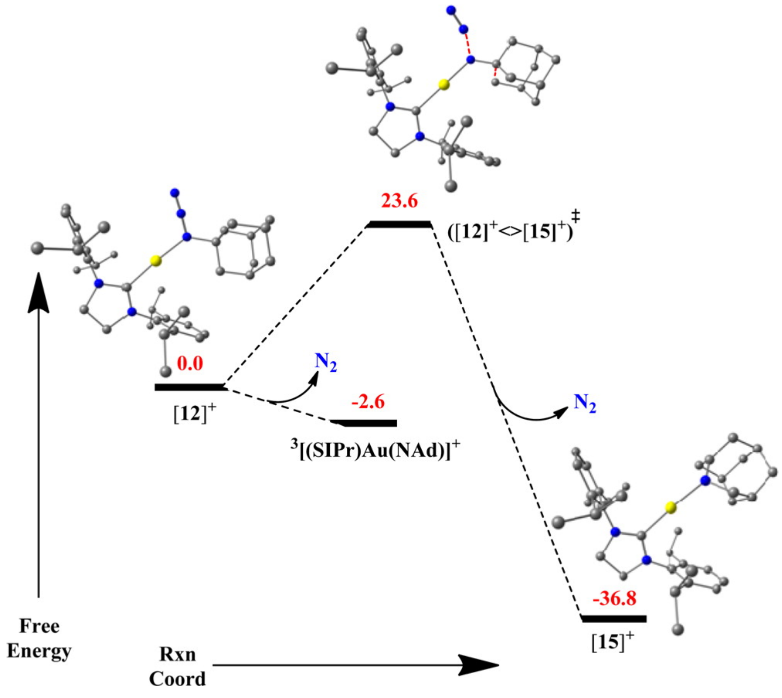
http://www.gaussian.com/g_whitepap/oniom_technote.htm

ONIOM publications



Gold-Mediated Expulsion of Dinitrogen from Organic Azides





Chandrakanta Dash, Muhammed Yousufuddin, Thomas R. Cundari, and H. V. Rasika Dias

J. Am. Chem. Soc., 2013, 135 (41), pp 15479–15488 DOI: 10.1021/ja406027x

Methane Monooxygenase

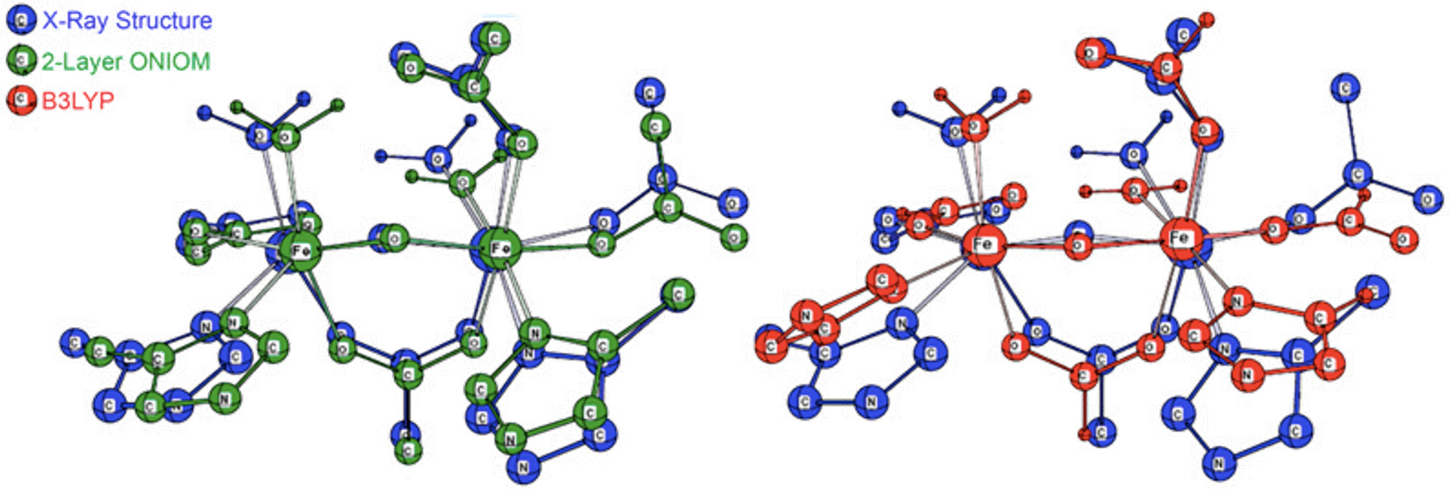


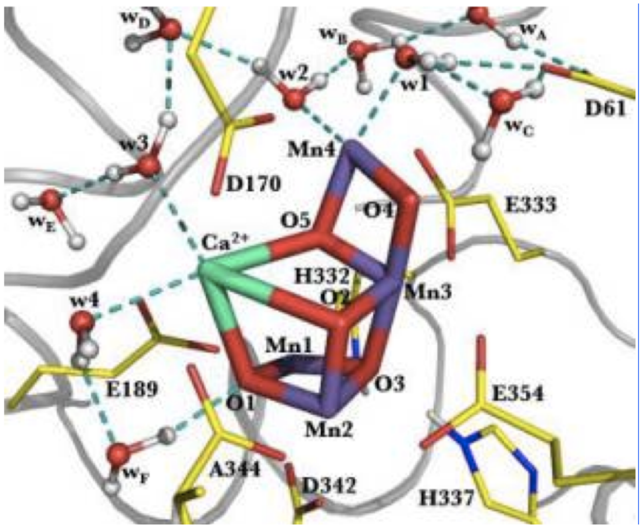
Figure 3. Comparison of the 2-Layer ONIOM (green, at left) **and B3LYP** (red, on the right) **Optimized Geometries with the Experimental X-Ray Structure** (blue)

https://gaussian.com/oniom_technote/

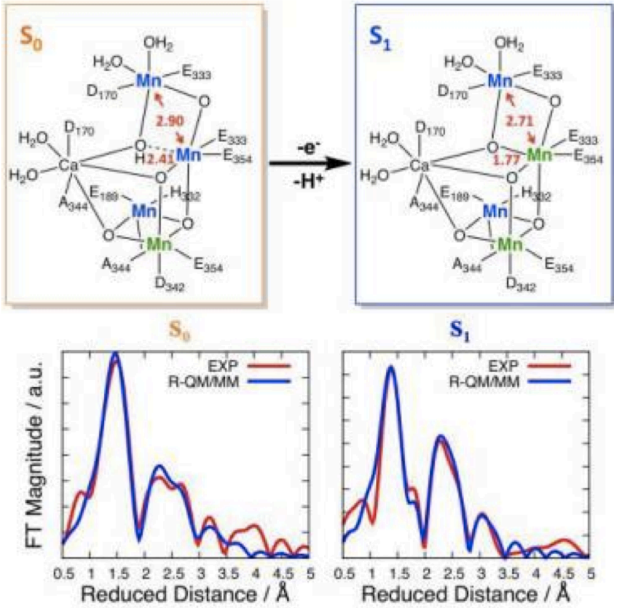
OEC Photosystem II

S_0-State Model of the Oxygen-Evolving Complex of Photosystem II

Rhitankar Pal, Christian F. A. Negre, Leslie Vogt, Ravi Pokhrel, Mehmed Zahid Ertem, Gary W. Brudvig, and Victor Salvador Batista

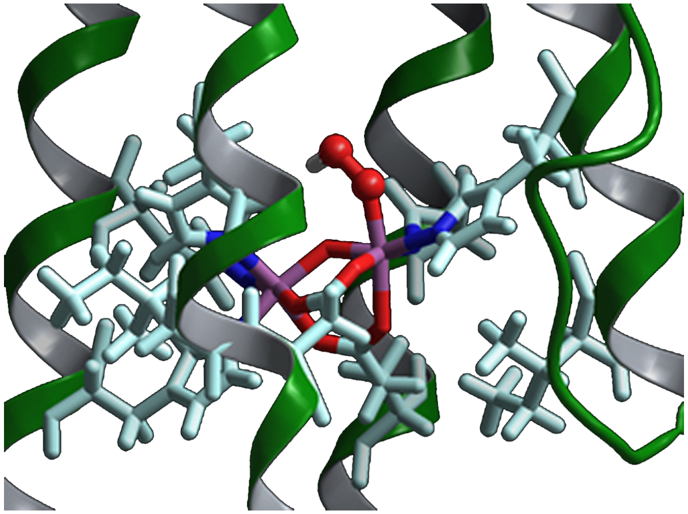


http://dx.doi.org/10.1021/bi401214v



Top: The structural changes induced by the S0->S1 transition. The distances Mn3-Mn4 and Mn3-O5 are shortened upon oxidation of Mn and deprotonation of the hydroxo bridge. Color key: Green MnIV; Blue MnIII. Bottom: Comparison of the experimental Fourier transform EXAFS spectra (red) and the calculated (blue) spectra of the S0 (left) and S1 (right) QM/MM models.

Schrödinger - QSite



The active site of the oxy form of Hemerythrin is is shown in tubes while the protein backbone is represented by ribbons, the dioxygen that binds reversibly to Hemerythrin is drawn in spheres bonded to the iron atom on the right. The QSite-predicted in vivo free energy of binding of - 5.2 kcal/mol is in remarkably good agreement with the experimental value of -7.3 kcal/mol, derived from the equilibrium constant of (2.5 ± 0.5)x10^5M-1 obtained from stopped-flow experiments carried out in solution). You do not need mm parameters for the QM portion of the molecule.