Vibrations in Free Radicals



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π -conjugated free radicals





Quantum electronic structure programs let us predict:

- Relative energies for isomers, reactants vs. products
- Geometries of reactants, products, intermediates, transition states

by solving molecular Schrödinger equation within Born-Oppenheimer approximation

• Harmonic vibrational frequencies to estimate IR spectra, also zero-point and thermal corrections to $\Delta_{rxn}G$.

Basis sets: how we construct the electronic wavefunctions

 Many-electron wavefunctions in molecules constructed from 2-electron or 1-electron molecular orbitals (MOs)

- MOs constructed as sums over atomic orbitals
- 1-electron atomic orbitals are $R_{n,l}(r) Y_{lm}(\theta,\phi)$ where Rn,l(r) decays as e^{-r}

• But 4-center integrals much easier with Gaussians than *e*^{-*r*} because can rewrite as two 2-center integrals.

Gaussian basis sets



Gaussian basis sets



Gaussian basis sets



basis set polarization functions



S р

| 100% | 95% |
|------|-----|
| 0 | 5% |

| 90% | 80% |
|-----|-----|
| 10% | 20% |

Methods: how we approximate the Schrödinger equation

| Molecular mechanics (MM) | Long-range forces; no esoteric bonding allowed |
|---|--|
| Hartree-Fock (HF) | Basic bonding; no dispersion or excited states |
| Density Functional Theory (DFT) | Often excellent; still no dispersion or excited states |
| Correlated methods (MP2,CI,QCISD,CC) | Excellent but expensive |

Vibrations in Free Radicals

HC₃O QCISD/6-311G(d,p) PES

Many conjugated free radicals have isomers related through **relocalization**, leading to **anharmonic** and **highly coupled** vibrational modes.





We want vibrational **energies** and **wavefunctions** for arbitrary, reduceddimensional (2D or 3D) potential energy surfaces of polyatomic molecules.

Do this by integrating nuclear Schrödinger equation (second-order partial differential equation, PDE) on potential energy surface.

Can do this by numerical integration. Many methods available.

Finite element method (FEM)

- PhD student Dong Xu selects FEM to expand this to higher dimensionality:
- Approximate the solution to the Schrödinger PDE (rather than approximating the PDE itself) by breaking the wavefunction into polyhedra, Each polyhedron is a localized basis function.
- Successively improve the wavefunction by an estimator for the errors at the boundaries.

FEMvib program



Works for **any** bounded potential energy surface, using orthogonal or non-orthogonal coordinates.

Verify this with several test cases...



n=2 state

FEMvib.









Lagris et al. (1997)

Tests all successful. Ready for a real problem.

3-D harmonic oscillator

 $V(x,y,z) = 0.5 x^2 + 0.72 y^2 + 0.845 z^2$

FEMvib solves eigenstate # 202 with $E_{calc} = 15.7505 \text{ vs.} E_{exact} = 15.7500$

We can also graph the wavefunctions...



3D SHO Eigvec #25 (2 1 1)



Ar-H₂O

Van der Waals complex with extremely anharmonic vibrational modes.



R = 3.4 A

 $R = 3.7 \, \text{A}$

Fully ab initio solution

- Calculated CCSD(T)/cc-pVTZ PES at ~500 points over symmetry-unique R=2.5-5Å, θ=0-π/2, φ=0-π.
- Use Dunning's correlation-consistent basis sets (with polarization functions) to extrapolate to complete basis set limit.
- Apply Counterpoise correction to basis set superposition error.

Lowest J=0 term energies (cm⁻¹) of Ar-H₂O.

stateAW2FEMstateAW2FEM $n=0 \Sigma(1_{01})$ 15.316.7 $n=2 \Sigma (0_{00})$ 61.959.1 $n=1 \Sigma (0_{00})$ 35.430.3 $n=0 \Sigma (2_{02})$ 74.165.5 $n=0 \Sigma (1_{11})$ 43.740.6 $n=0 \Sigma (2_{12})$ 75.971.1 $n=1 \Sigma (1_{01})$ 49.750.7 $n=1 \Sigma (1_{11})$ 78.173.3 $n=0 \Sigma (1_{10})$ 57.852.9 $n=2 \Sigma (1_{01})$ 82.180.2

AW2 = Cohen & Saykally from experimental data FEM = this work

Ar-H₂O Wavefunctions





n=0 Σ(0₀₀)

n=0 Σ(1₁₀)

Ar-H₂O Wavefunctions





n=0 Σ(0₀₀)

 $n=0 \Sigma(1_{10})$

Wait a minute...

Ar-H₂O Wavefunctions



| n=0 Σ(0 ₀₀) | n=0 Σ(1 ₁₀) |
|-------------------------|-------------------------|
|-------------------------|-------------------------|

Wait a minute... where's the rest of the wavefunction?

But then why the right answer?

The vibrational Schrodinger equation

$$-\nabla^2 u + V u - \varepsilon u = 0$$

is given the following weak formulation

$$\int_{\Omega} \nabla v \cdot \nabla u \, d\Omega - \int_{\Gamma} v \, \nabla u \cdot \hat{\mathbf{n}} \, d\Gamma + \int_{\Omega} v \left[\left(V - \varepsilon \right) u \right] d\Omega = 0.$$

and apply Dirichlet boundary condition

$$u, v = 0$$
 on $\partial \Omega = \Gamma$

to eliminate second term

But actually we are requiring only that *du* is zero; not sufficiently restrictive.

Particle in 1D box analogy:



This is not a problem for most of our radical systems.





























Transition state











New HC₃O surface

- $\Box \theta$ (HCC), θ (CCO), R_1 - R_2
- QCISD coupled cluster method
- cc-pVDZ basis set
- Still need to apply CBS extrapolation













Other systems: ZnCl₂+



Wenli Zou and James Boggs, UT Austin

Other systems: ZnCl₂+



Other systems: ZnCl₂+

| (v_1, v_2, v_3) | Energy (cm ⁻¹) |
|-------------------|----------------------------|
| (0,0,0) | 176 |
| (0,0,1) | 281 |
| (1,0,0) | 409 |
| (1,0,1) | 537 |
| (0,0,2) | 596 |
| (2,0,0) | 673 |
| (0,0,3) | 781 |
| (2,0,1) | 826 |
| (1,0,2) | 873 |
| (3,0,0) | 953 |

Assignment of traditional quantum numbers becomes ambiguous after a few excitations, but the experimental observables (energies, vibrational amplitudes, etc.) still interpretable in this analysis.

Other systems: H transfer catalysis

Douglas Grotjahn & group

Dalton Transactions

An international journal of inorganic chemistry

Grotjahn

Bifunctional catalysts and related

complexes: structures and properties

RSCPublishina

www.rsc.org/dalton

Number 46 | 14 December 2008 | Pages 6485-6648



heterobimetallic complexes as

materials

precursors for ceramic and magnetic

1477-9726/2008(46:1-W



















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Reaction diagram for hydration



Conclusions

- New program for modeling complex vibrational quantum mechanics of polyatomics working
- Just now getting back to the radicals that inspired the work

Future work

- Periodic coordinates
- Correct for zero-point energy variations in other coordinates
- Finish web interface

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