

Constructing effective hamiltonians for multiple electronic states and their intersections

(With a summary of earlier work on PES fitting)

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Potential energy surfaces and their uses

Fitted potential energy surfaces

Illustrations

Problems and Outlook (in 2009)

Conical Intersection, diabatic states

Potential energy surfaces

Potential Energy Surface (PES): $V = V(X)$

X : Collective ($3N$) nuclear coordinates.

Electron dynamics is gone. This is the Born-Oppenheimer (adiabatic) approximation.

Also of interest, the dipole moment surface (DMS) $\mathbf{d}(X)$ (a vector quantity) and other properties.

Fundamentally $V(X)$, $\mathbf{d}(X)$, etc., are obtained by expensive electronic structure calculations. Our work is concerned with analytical, fitted surfaces that are cheap to evaluate.

Molecular dynamics: “ $F=ma$ ”

N atoms; classical nuclei, positions $x(i)$, $1 \leq i \leq N$.

Interaction potential $V(X)$ ($X \in \mathbf{R}^{3N}$).

Force $F = -\nabla V$.

$$\frac{\partial^2 x(i)}{\partial t^2} = -\frac{1}{m_i} \frac{\partial V}{\partial x(i)}$$

Applications range from small molecule reaction dynamics to protein folding.

Molecular spectroscopy

Eigenvalue problem $H\Psi = E\Psi$:

$$-\sum_i \frac{\hbar^2}{2m_i} \Delta_i \Psi(X) + V(X)\Psi(X) = E\Psi(X)$$

Configuration interaction approach (Hartree products):

$$\Psi(X) = \sum_{\alpha} c_{\alpha} \Psi_{\alpha}(X)$$

$$\Psi_{\alpha}(X) = \prod_i \psi_{\alpha(i)}^{(i)}(x(i))$$

This provides the ro-vibrational spectrum. Tractable for small molecules: e.g. $2(\text{H}_2\text{O})$, CH_3OH ; up to 9 atoms in our work.

Diffusion Monte Carlo

Ground state wavefunction: $H\Psi = E_0\Psi$.

$$-\sum_i \frac{\hbar^2}{2m_i} \Delta_i \Psi(X) + V(X)\Psi(X) = E_0\Psi(X)$$

Steady state for reaction-diffusion equation:

$$\frac{\partial \Psi}{\partial t} - \sum_i \frac{\hbar^2}{2m_i} \Delta_i \Psi(X) + V(X)\Psi(X) = E_0\Psi(X)$$

Can be solved in many dimensions using random walk with birth and death processes.

Result is ground state energy E_0 ; plus sample from the ground state wavefunction. (Sample $|\Psi^2|$ via descendant weighting.)

Quantum statistics

Partition function $Z(\beta) = \text{tr}(e^{-\beta H})$. Thermal averages:

$$\langle A \rangle_{\beta} = \frac{1}{Z(\beta)} \text{tr}(Ae^{-\beta H})$$

Use $e^{-\beta H} = (e^{-(\beta/n)H})^n$; $H = T + V$; $n \rightarrow \infty$. Let $\beta_n = \beta/n$,
 $\omega_n = 1/\beta_n \hbar$;

$$V_n(\mathbf{X}) = \sum_i (V(X_i) + \frac{1}{2} m \omega_n^2 (X_{i+1} - X_i)^2)$$

$$Z_n(\beta_n) = \int e^{-\beta_n V_n(\mathbf{X})} d\mathbf{x}$$

Path Integral Monte Carlo.

Ring Polymer Molecular Dynamics

Due to David Manolopoulos (Oxford). PIMC plus time evolution.
Classical hamiltonian:

$$H_n(x, p) = V_n(x) + \sum_i \frac{p_i^2}{2m}$$

$$\frac{dx}{dt} = \frac{\partial H_n}{\partial p}, \quad \frac{dp}{dt} = -\frac{\partial H_n}{\partial x}$$

Seen as a model for calculating the quantum Kubo correlation function.

$$\tilde{c}_{A,B}(t) = \frac{1}{\beta Z(\beta)} \int_0^\beta \text{tr}(e^{-(\beta-\lambda)H} A(0) e^{-\lambda H} B(t)) d\lambda$$

Quantum scattering

Time-dependent Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \Psi(X, t) = H\Psi(X, t)$$

Wavepacket propagation in an unbounded domain. Application to reaction dynamics is pretty much limited to 4-atom systems.

Reminder: PES and DMS, coordinates

Born-Oppenheimer PES and DMS: $V = V(X)$, $\mathbf{d} = \mathbf{d}(X)$.

X : Collective ($3N$) nuclear coordinates.

Quadrupole moment, polarizabilities, etc., also of interest.

For applications we want accurate fitted PES, DMS, etc.. Requires function fitting in many dimensions.

Important earlier work: [J. N. Murrell et al., *Molecular Potential Energy Functions*, Wiley, 1984]. 3- and 4-atom systems.

Choice of coordinates

Considerations

- ▶ V is invariant under the point group symmetries: translation, rotation, reflection. Thus, $3N - 6$ independent coordinates.
- ▶ V is invariant under permutations of like nuclei.

Use functions of the internuclear distances, $r(i,j) = \|\mathbf{x}(i) - \mathbf{x}(j)\|$.

For example, let $y(i,j) = \exp(-r(i,j)/\lambda)$; hence vector $y \in \mathbf{R}^d$, $d = N(N - 1)/2$; and then $V = p(y)$.

Polynomial p must be invariant under permutations of like nuclei.

Permutation symmetry group

Say N nuclei, indexed by $\{i : 1 \leq i \leq N\}$.

Say K different kinds; hence partition $N = n_1 + \dots + n_K$.

\Rightarrow Group $G = \text{Sym}(n_1) \times \dots \times \text{Sym}(n_K)$.

Non-standard representation. Variables $y \in \mathbf{R}^d$ ($d = N(N-1)/2$); components $y(i, j)$ ($i \neq j$); $y(i, j) = y(j, i)$. Permutation $\pi \in G$:

$$\pi : (\pi y)(i, j) = y(\pi^{-1}i, \pi^{-1}j)$$

Need polynomials of $y \in \mathbf{R}^d$ invariant under $\text{Sym}(n_1) \times \dots \times \text{Sym}(n_K)$ acting on \mathbf{R}^d .

Dipole moment also requires covariants $\mathbf{R}^d \rightarrow \mathbf{R}^N$.

Quadrupole moment, polarizability require further covariants.

\Rightarrow Invariant theory of finite groups.

Invariants of finite groups - Introduction

Easy case: Polynomials on \mathbf{R}^n invariant under $\text{Sym}(n)$.

Representation $(\pi p)(x) = p(\pi^{-1}x)$ for $x \in \mathbf{R}^n$; $(\pi^{-1}x)_i = x_{\pi i}$.

Generated by the elementary monomials:

$$p_k(x) = \sum_i x_i^k$$

Every invariant polynomial $f(x)$ has a *unique* representation in the form $f(x) = \text{poly}(p_1(x), \dots, p_n(x))$.

[Computational cost $O(1)$ per term; compare with $O(n!)$ per term for symmetrized monomial basis.]

Just as easy: Polynomials on $\mathbf{R}^{n_1+\dots+n_K}$ invariant under $\text{Sym}(n_1) \times \dots \times \text{Sym}(n_K)$ in the “natural” representation.

Invariants of finite groups - More general

Not easy: $\text{Sym}(n_1) \times \cdots \times \text{Sym}(n_K)$ in our not so natural representation on \mathbf{R}^d , $d = N(N - 1)/2$.

Need invariant polynomials for a finite group G acting on a finite dimensional vector space (say \mathbf{R}^n) (characteristic 0).

[Harm Derksen and Gregor Kemper, *Computational Invariant Theory*, Springer Verlag, 2002].

Cohen-Macaulay property: There exists a family of n *primary generators*, invariant polynomials p_i ($1 \leq i \leq n$), together with a family of *secondary generators*, invariant polynomials q_α , such that every invariant polynomial $f(x)$ has a *unique* representation in the form $f(x) = \sum_{\alpha} \text{poly}_{\alpha}(p_1(x), \dots, p_n(x))q_{\alpha}(x)$.

Invariants of finite groups - Example

A: Case of $G = \text{Sym}(2)$ acting on \mathbf{R}^2 generated by reflections:
 $(x, y) \mapsto (x, -y)$. May choose $p_1(x, y) = x$, $p_2(x, y) = y^2$, and
 $q_1(x, y) = 1$. Then:

$$f(x, y) = \text{poly}_1(x, y^2)$$

B: Case of $G = \text{Sym}(2)$ acting on \mathbf{R}^2 generated by inversions:
 $(x, y) \mapsto (-x, -y)$. May choose $p_1(x, y) = x^2$, $p_2(x, y) = y^2$, and
 $q_1(x, y) = 1$, $q_2(x, y) = xy$. Then:

$$f(x, y) = \text{poly}_1(x^2, y^2) + \text{poly}_2(x^2, y^2)xy$$

Invariants of finite groups - Larger example

Example for a molecular group, the X₅Y₂ molecule.

$G = \text{Sym}(5) \times \text{Sym}(2)$ acting on \mathbf{R}^{21} (21 internuclear distances).

There are 21 primary invariants: 3 of degree 1, 5 of degree 2, 3 of degree 3, 4 of degree 4, 3 of degree 5, 2 of degree 6 and 1 of degree 10. The number of secondary invariants at degrees 0..9 is 1, 0, 1, 12, 39, 113, 338, 932, 2402, 5678.

MAGMA computer algebra system

Developed at the University of Sydney, and elsewhere.

Includes representation theory of finite groups.

- ▶ W. Bosma and J. Cannon: The Magma Handbook. (13 volumes, \simeq 5800 pages in 2017.)
- ▶ Gregor Kemper and Allan Steel (1997) *Some Algorithms in Invariant Theory of Finite Groups*.

Use MAGMA to obtain primary and secondary invariants.

Convert MAGMA output to Fortran code.

Done this for almost all molecular symmetry groups for at most 9 atoms.

MAGMA output

Fragment of output for X5Y2.

```
pv(205) = SYM d(i0,i1)*d(i0,j0)^5
pv(206) = SYM d(i0,i1)^4*d(i0,j0)*d(i1,j0)
pv(207) = SYM d(i0,i1)^3*d(i0,i2)*d(i0,j0)*d(i1,j0)
pv(208) = SYM d(i0,i1)^2*d(i0,i2)^2*d(i0,j0)*d(i1,j0)
pv(209) = SYM d(i0,i1)*d(i0,i2)^3*d(i0,j0)*d(i1,j0)
pv(210) = SYM d(i0,i2)^4*d(i0,j0)*d(i1,j0)
pv(211) = SYM d(i0,i1)^2*d(i0,i2)*d(i1,i2)*d(i0,j0)*d(i1,j0)
pv(212) = SYM d(i0,i1)*d(i0,i2)^2*d(i1,i2)*d(i0,j0)*d(i1,j0)
pv(213) = SYM d(i0,i2)^3*d(i1,i2)*d(i0,j0)*d(i1,j0)
pv(214) = SYM d(i0,i2)^2*d(i1,i2)^2*d(i0,j0)*d(i1,j0)
pv(215) = SYM d(i0,i1)^2*d(i0,i2)*d(i0,i3)*d(i0,j0)*d(i1,j0)
pv(216) = SYM d(i0,i1)*d(i0,i2)^2*d(i0,i3)*d(i0,j0)*d(i1,j0)
pv(217) = SYM d(i0,i2)^3*d(i0,i3)*d(i0,j0)*d(i1,j0)
pv(218) = SYM d(i0,i1)^2*d(i1,i2)*d(i0,i3)*d(i0,j0)*d(i1,j0)
```

Reduction in size of the basis

Example, X5Y2 (H_5O_2^+ , H_5C_2 , H_5C_2^+); single expansion.

$N = 7$, $d = 21$ ($N(N - 1)/2$); polynomials up to degree 7.

Using symmetry, approximation space has dimension 8,717.

Without using symmetry, dimension $\binom{28}{7}$, = 1,184,040.

Least squares system: ~ 50000 equations in ~ 8717 unknowns.

Can do larger problems using single expansion; even 9-atom systems with sufficient symmetry ($3(\text{H}_2\text{O})$, $\text{H}_4\text{C}_3\text{O}_2$). Can anyway use many-body expansion.

Many-body expansion

Example for H_3C_2 complex:

$$V_{\text{all}} = V_{\text{H}} + V_{\text{C}} + V_{\text{H}_2} + V_{\text{HC}} + V_{\text{C}_2} + V_{\text{H}_3} \\ + V_{\text{H}_2\text{C}} + V_{\text{HC}_2} + V_{\text{H}_3\text{C}} + V_{\text{H}_2\text{C}_2} + V_{\text{H}_3\text{C}_2}$$

in which, for example

$$V_{\text{H}_2\text{C}} = \sum_{\substack{i,j \in \text{"H"} \\ i < j}} \sum_{k \in \text{"C"}} f_{\text{H}_2\text{C}}(r_{ij}, r_{ik}, r_{jk})$$

and then $f(x) = p(y(x)) \text{damp}(x)$ and, component-wise, for example, $y(x) = \exp(-x/\lambda)$

Coefficients of each such p from weighted least squares.

Also applied to water clusters, but in that work each H_2O is one "body".

Sampling and fitting

We are sampling a space of $3N - 6$ dimensions. It is an iterative procedure.

Create tentative surface, sample from molecular dynamics (MD) runs, apply random perturbations, etc.

Sample from diffusion Monte Carlo (DMC) runs.

Sample from MD at higher temperature, from DMC at reduced mass

Newton search for stationary configurations; sample around those.

Include points from a Multimode mesh (ro-vibrational spectroscopy calculation).

Create several fitted surfaces, look for configurations where the difference is large, add to the sample.

Etc.. Start it all with relatively robust DFT (e.g., B3LYP); then move on to RCCSD(T) or other fundamental method that needs more care

Tunneling splitting in malonaldehyde

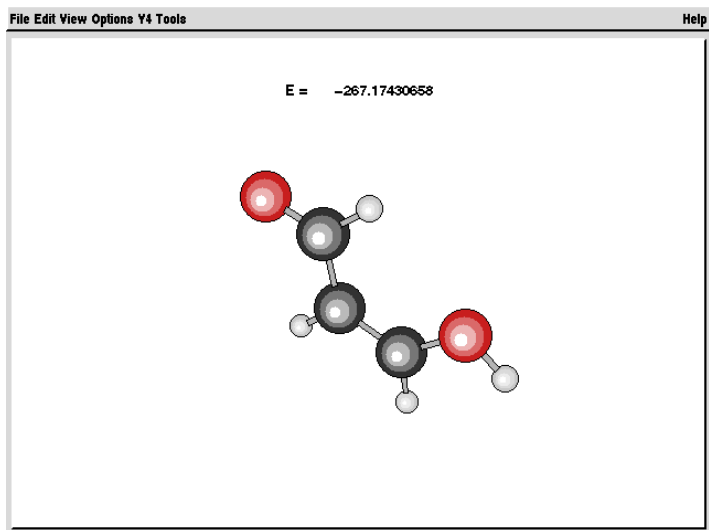
[Yimin Wang, Bastiaan J. Braams, Joel M. Bowman, Stuart Carter, and David P. Tew, J. Chem. Phys. **128** (2008).]

Ab initio by David Tew: CCSD(T) near basis set limit with F_{12} correction. H-transfer barrier 4.1 kcal/mol.

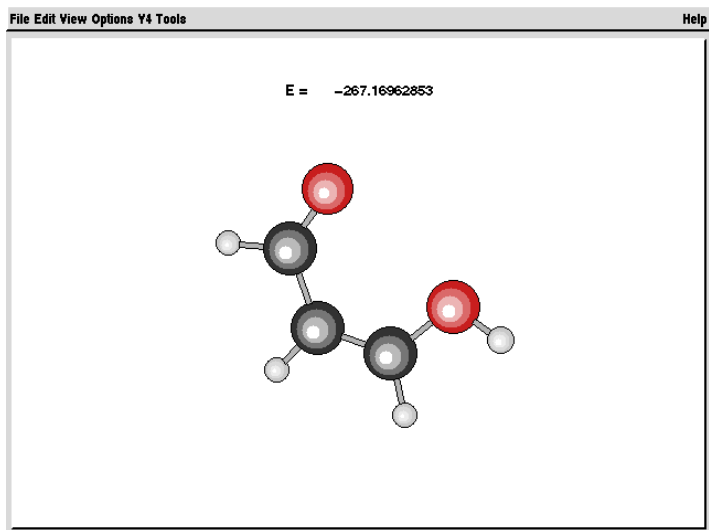
Calculated splitting (DMC) for H: 22/cm; uncertainty 3/cm; measured 21.6/cm. For D: 3/cm; uncertainty 3/cm; measured 2.9/cm.

Highly accurate surface for tunneling splitting; but we also have a DFT surface for higher-energy dynamics – see pictures below.

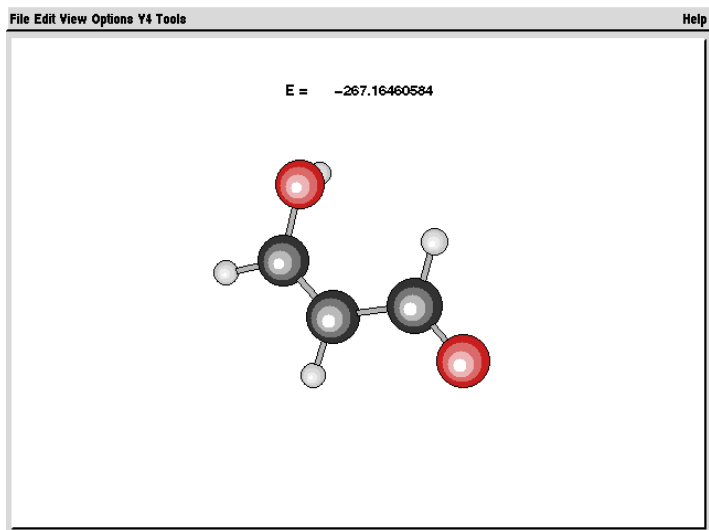
Malon-3



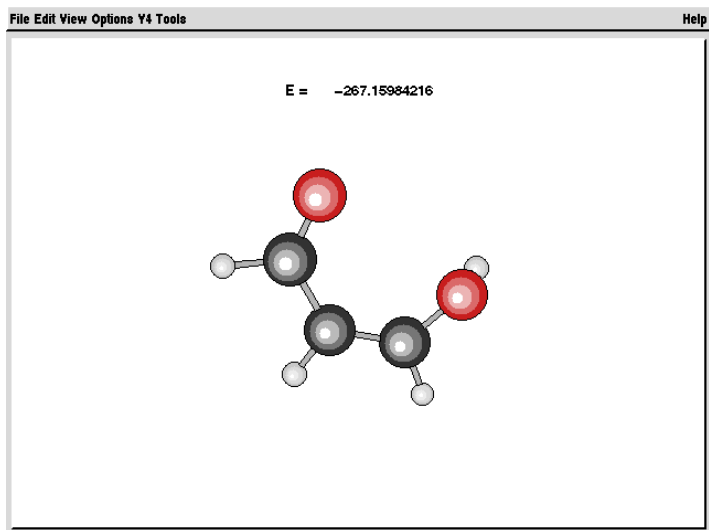
Malon-4



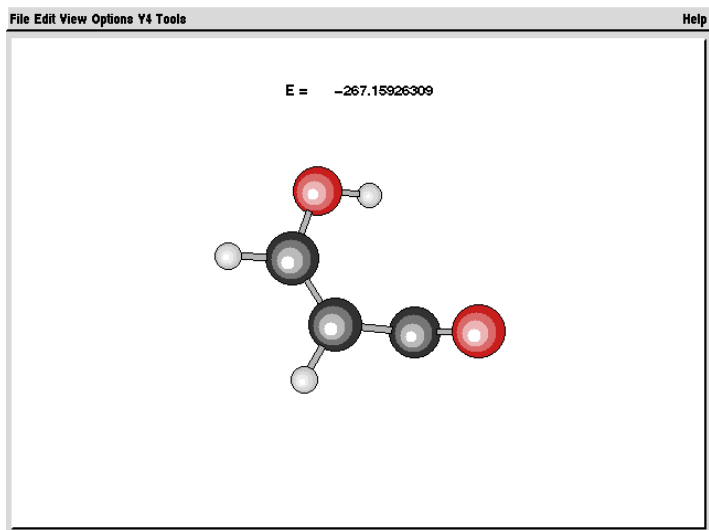
Malon-5



Malon-6



Malon-7



Problems: It doesn't scale

Larger molecules: PES for 3 atoms, many options. For 4 atoms, John Murrell, systematic expansion, late 1970's. For 5-9 atoms, our present work; also Mike Collins, Shepard interpolation.

Global expansion in Morse variables not beyond $\simeq 9$ atoms.

Many-body expansion may not converge; truncated MBE may not be accurate – it depends on the system.

But... Very successful now for water clusters.

... It isn't transferable

Every molecule has its own PES.

Need proper role for fragment potentials. Overlapping fragments; inclusion - exclusion counting; make it work also for reactions, charged systems, singlet and triplet surfaces.

On the other hand... we get high accuracy; not achieved with any more general models (mechanical models, semi-empirical models).

... It isn't even global

Full-dimensional, yes. Beautiful for spectroscopy. Very good for dissociation experiments. Sufficiently global for small reactions.

Reactions, large systems much more difficult. CH_3COCH_3 (Acetone) straight photo-dissociation we could do; $\text{CH}_3 + \text{CH}_3\text{CO}$ reaction, not with the present approach.

The competition might be reparameterized semiempirical work.

... The underlying data have their own problems

PES/DMS should fit ab initio, but ab initio may fail.

We rely much on interpolation between fragment data and complex region data.

Multireference CI as benchmark, but very expensive for database.

... Born-Oppenheimer may not be valid

We have not addressed conical intersection issues (coalescence of eigenvalues). Single global fit present style to the lower surface can't be accurate.

Need to fit diabatic potential energy matrix W , globally. It may be covariant (not invariant) under permutations of nuclei. It is not obvious to what data such W should be fitted.

... Need to provide analytical gradients

If $f : V \rightarrow \mathbf{R}$ is an invariant polynomial then $g = \nabla f$ is a covariant, $g : V \rightarrow V^\dagger$.

Say $f(x) = \sum_{\alpha} \text{poly}_{\alpha}^{(f)}(p(x))q_{\alpha}(x)$ and
 $g(x) = \sum_{\alpha} \text{poly}_{\alpha}^{(g)}(p(x))r_{\alpha}(x)$.

Coefficients of $\text{poly}^{(g)}$ depend linearly on those of $\text{poly}^{(f)}$ and the map can be pre-computed; hence optimally efficient gradient.
Hessians are the same story, just a different covariant.

New interest: regular solids

Assume general 3d periodic lattice, N atoms per unit cell.

Potential energy is invariant under translation, rotation, reflection;
 $3N + 3$ intrinsic parameters.

(Case of $N = 1$: 6 inner products among lattice basis vectors.)

Specify the lattice by matrix $L = (\mathbf{a}, \mathbf{b}, \mathbf{c})$; a general lattice point is Lu for u in the unit lattice Z^3 .

Potential energy is invariant under change of lattice basis:

$L \rightarrow LM$, $M \in SL(3, Z)$ (an infinite group). The 6 inner products are not nice variables under this transformation.

Regular solids, cont'd

Good variables for the case of $N = 1$: Oscillatory lattice sums; exponent $-n$. For $k \in \{0, 1\}^3$ let

$$f_k(L) = \sum_{u \neq 0} (-1)^{k^T u} \|Lu\|^{-n}$$

(define by analytic continuation or Ewald summation if needed).

Oscillatory: $k \neq 0$; hence 7 variables (redundant coordinates).

They are covariant under $SL(3, Z)$, but really only the subgroup $SL(3, F_2)$ matters.

Back to invariants of finite groups. 168 elements in this case. A polynomial expansion to total degree ≤ 9 has only 184 terms.

Conical intersections

Real symmetric generalized eigenvalue problem of order n :

$$H.x = K.x.\lambda, x^T.K.x = 1; x \in R^n.$$

H and K depend smoothly on parameters $s \in R^d$.

Multiple states: $H.X = K.X.\Lambda, X^T.K.X = \text{Id}_n$.

Eigenvalue coalescence happens generically on a surface of codimension 2 (dimension $d - 2$), called the seam of intersection.

Gradient is discontinuous there.

Dimension counting argument for seam of intersection

Real symmetric matrices of order n : Space of dimension $n(n+1)/2$.

Diagonal matrices of order n , space of dimension n ; Lie group $SO(n)$, space of dimension $n(n-1)/2$; adds up to $n(n+1)/2$.

Simple eigenvalue coalescence: Diagonal matrices space of dimension $n-1$; Lie group $SO(n)/SO(2)$ of dimension $n(n-1)/2 - 1$; adds up to $n(n+1)/2 - 2$.

Complex hermitian case: eigenvalue coalescence generically on space of codimension 3.

Real symmetric triple eigenvalue coalescence generically on space of codimension 5.

Fitting a hamiltonian; what's the problem?

Eigenvalues Λ are not smooth functions.

Transformation properties of Λ are clear: scalar (invariant) under $SO(3)$ and under permutation of identical nuclei.

Effective hamiltonian and mass matrix H, K (of small order) should be smooth functions, suitable for fitting.

Transformation properties of H (and K) are a priori unclear. Could be any orthogonal (or unitary) representation of $SO(3)$ and of $Sym(k)$; could involve many irreducible representations.

Fitting a hamiltonian will require a starting guess, then continuous optimization. The (discrete) invariance properties remain frozen during the optimization.

Need to decide: (a) What are the transformation properties of our fitted H and K ; (b) What are the training data?

(Alternative, not pursued here: combinatorial search for the correct transformation properties.)

Hamiltonian with proper transformation properties

At first we do not know how to guess the transformation properties of a small effective hamiltonian that gives us the diabatic states.

We do know a very large hamiltonian that transforms correctly: Full configuration interaction (CI) on a basis of atomic orbitals at fixed spatial orientation. No Hartree-Fock pre-stage!

We know moderately large hamiltonians that transform correctly and that are not completely off-base. Truncated CI on a minimal basis of atomic orbitals at fixed spatial orientation.

We can guess a structure for even smaller hamiltonians: minimal basis of atomic wavefunctions: 1s only on H; 1s, 2s, 2p on B, C, N, O, F. (Two functions for H, 15 functions for C, O.) Product states (at selected spin and spatial symmetry) for small molecules.

Fitting a Hamiltonian

Manifold M , fine space $V = R^n$, coarse space $W = R^m$, restriction map $P : V \rightarrow W$, fine space Hamiltonian $H(s : s \in M)$, mass matrix $K(s : s \in M)$; hence generalized eigenproblem

$$H.X = K.X.\Lambda, \quad X^T.K.X = \text{Id}_k;$$

Then $X^T.H.X = \Lambda$. Now define H', K' as operators on W to reproduce Λ . Let $Y = P.X$ and define $Q = X.Y^+$ where Y^+ is a pseudo-inverse: $Y^+ = (Y^T.Y)^{-1}.Y^T$; $Y^+.Y = I_k$.

Let

$$H' = (Y^+)^T.\Lambda.Y^+, \quad K' = (Y^+)^T.Y^+$$

Then $H'.Y = K'.Y.\Lambda$. Operators $H'(s : s \in M)$ and $K'(s : s \in M)$ on the coarse space are objects for fitting.

Fitting a Hamiltonian, continued

Embellishment (important): We have commuting operators H , S ; so $H.K^{-1}.S = S.K^{-1}.H$.

Now solve the joint problem: $H.X = K.X.\Lambda$, $S.X = K.X.\Sigma$.

Assume that S has discrete spectrum with high degeneracy. (S represents angular momentum, spin, etc..)

Must retain in Λ not simply the k lowest eigenvalues, but rather the k_i lowest eigenvalues for each block σ_i in Σ .

Alternative approach (not developed here): Instead of fitting the lowest eigenvalues, fit a thermal density matrix

$$\Gamma = X.\exp(-\beta\Lambda).X^T.$$

... To be continued!

Thank you for your attention