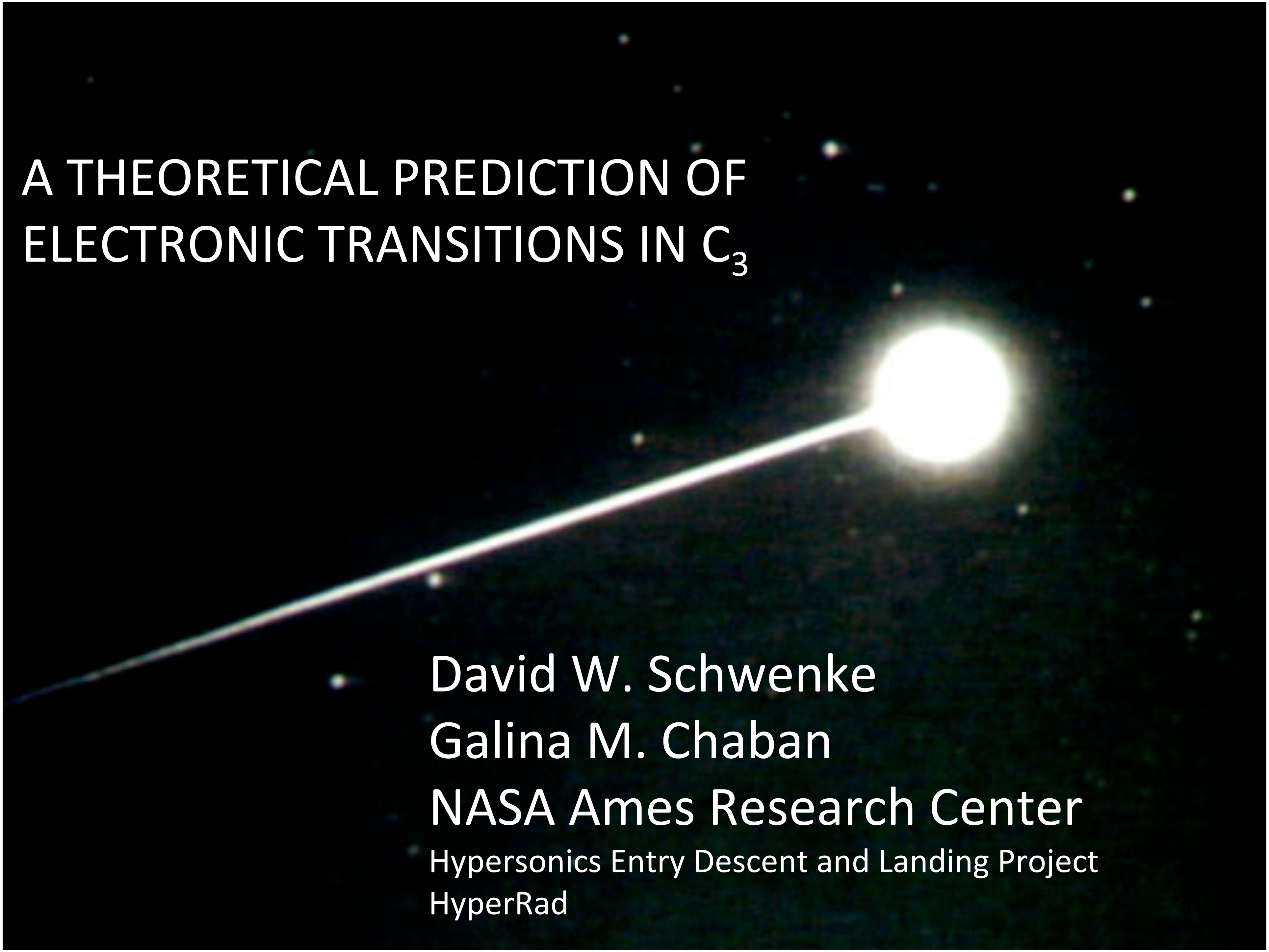

A THEORETICAL PREDICTION OF ELECTRONIC TRANSITIONS IN C_3

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Theoretical Methods

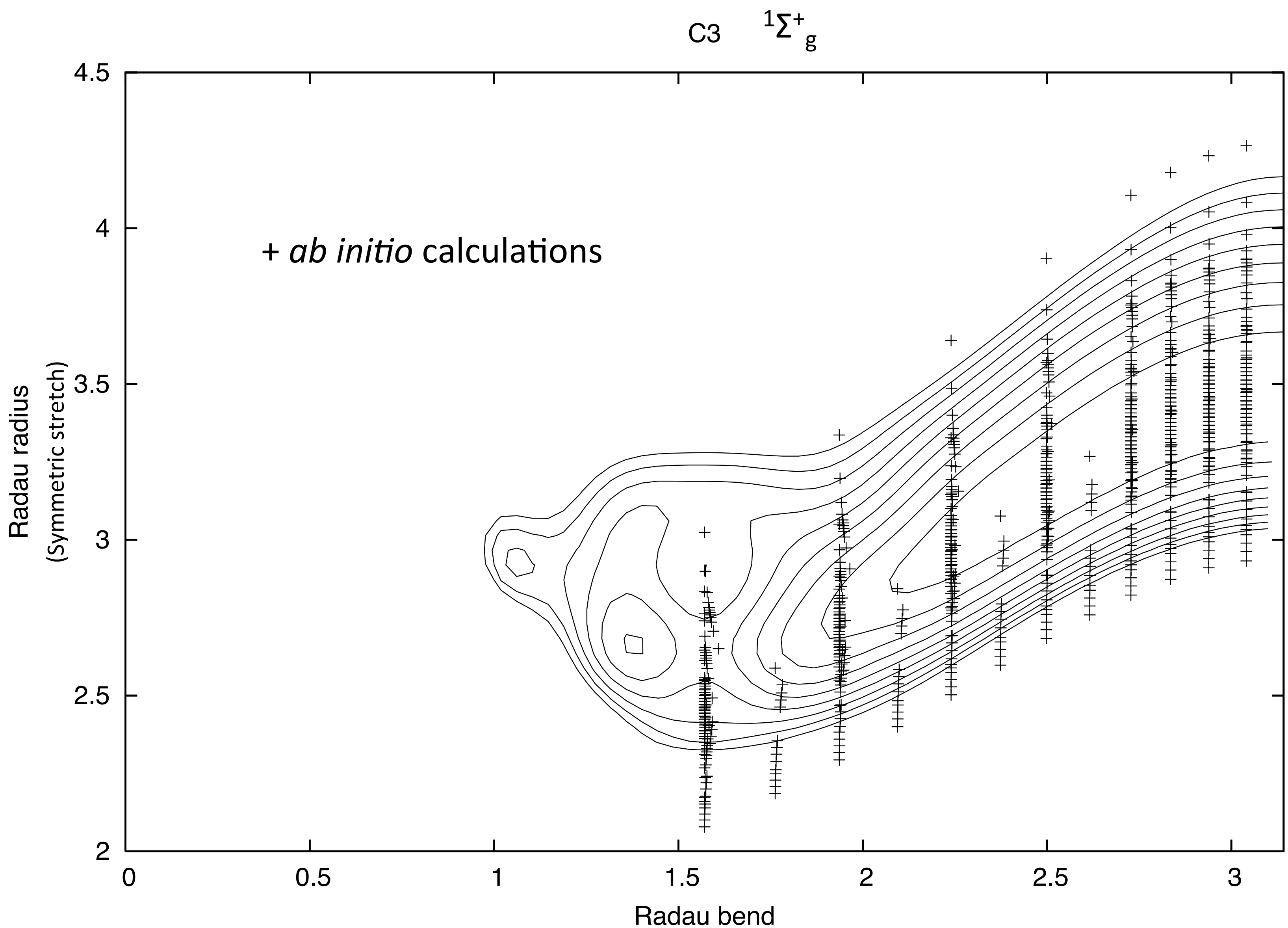
- MOLPRO
- aug-cc-pVTZ
- MCHF
  - FORS or restricted active space
  - dynamic weights
- icMRCI
  - ACPF for ground state
  - projected state method

Summary of States and challenges…

- Ground state
  - $^1\Sigma^+_g$
    - PES curvature
- First excited states
  - $^1\Pi_u$
    - BO breakdown
- VUV state(s)
  - $^1\Sigma^+_u$
    - avoided crossings

Vibrational Coordinates

- Orthogonal : simplest KE
  - Jacobi or Radau
- Nonorthogonal : complicated KE
  - Can optimize


C3 $^1\Sigma^+_g$
+ *ab initio* calculations
Radau radius
(Symmetric stretch)
Radau bend
4.5
4
3.5
3
2.5
2
0
0.5
1
1.5
2
2.5
3

$^1\Pi_u$ state

- Coupled to $^3\Sigma^+_u$ through spin-orbit
- Born-Oppenheimer breakdown terms include
  - $L^2_z/\sin^2\theta$
    - Renner-Teller Effect

Need KE with all bits and pieces

- In space frame $\vec{J} = \vec{R} + \vec{L} + \vec{S}$
- In body frame $\vec{R} = \vec{J} + \vec{L} + \vec{S}$
  - anomalous commutation relations…

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Ye Olde Quantum Mechanix	fly by seat of pants
Modern Quantum Mechanics	$\left(Rm_R Lm_L \middle| RLJM \right)$

Coupled spin-electronic-ro-vibrational wavefunctions

$$\Psi^{JMP}_{\Upsilon\kappa S\Sigma\rho}$$
$$= \left[\frac{2J+1}{4\pi(1+\delta_{\Upsilon 0}\delta_{\Sigma 0})}\right]^{\frac{1}{2}} \left\{ f_\kappa(\tilde{\boldsymbol{\omega}}) \mathscr{D}^{(J)}_{\Upsilon+\Sigma\, M}(\alpha^{LB}\beta^{LB}\gamma^{LB}) \bar{\Theta}_{S\Sigma\rho}(\tilde{\boldsymbol{x}};\tilde{\boldsymbol{\omega}}) \right.$$
$$\left. + P\xi_\rho(-1)^{J+S+\Upsilon} f_\kappa(\sigma_{xz}\tilde{\boldsymbol{\omega}}) \mathscr{D}^{(J)}_{-\Upsilon-\Sigma\, M}(\alpha^{LB}\beta^{LB}\gamma^{LB}) \bar{\Theta}_{S-\Sigma\rho}(\tilde{\boldsymbol{x}};\tilde{\boldsymbol{\omega}}) \right\}$$

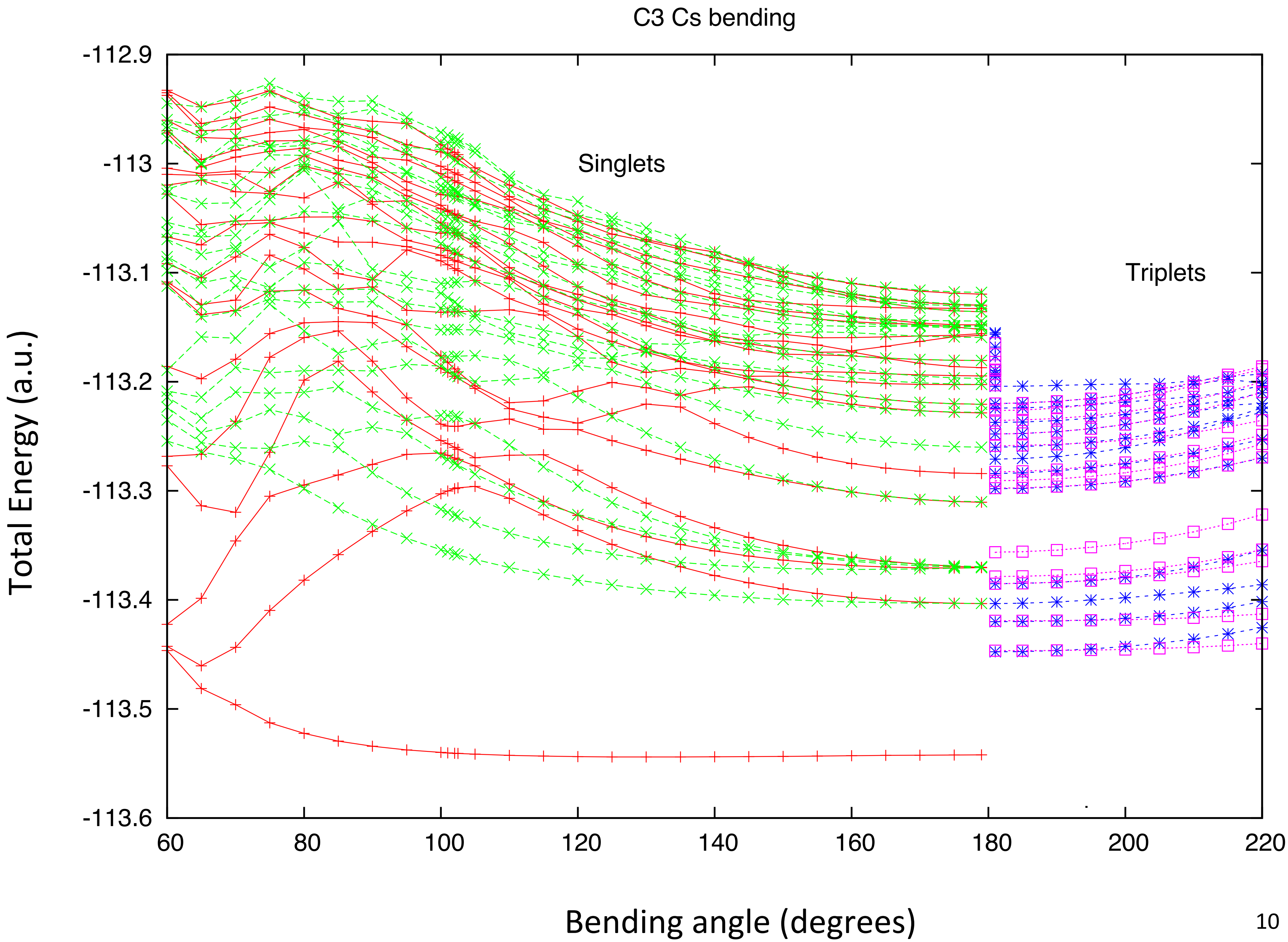
$$\left\langle \Upsilon\rho S\Sigma J \middle| \hat{R}^{bfn}_x \middle| \Upsilon'\rho' S\Sigma' J \right\rangle = -\delta_{\Upsilon\Upsilon'\pm 1}\delta_{\rho\rho'}\delta_{\Sigma\Sigma'}\tfrac{1}{2}\sqrt{J(J+1)-(\Upsilon+\Sigma)(\Upsilon'+\Sigma')}$$
$$+\delta_{\Upsilon\Upsilon'}\delta_{\Sigma\Sigma'}\tfrac{1}{2}\langle\rho S|L_+ + L_-|\rho' S\rangle + \delta_{\Upsilon\Upsilon'\pm 1}\delta_{\Sigma\Sigma'\mp 1}\delta_{\rho\rho'}\tfrac{1}{2}\sqrt{S(S+1)-\Sigma\Sigma'}$$

$$\left\langle \Upsilon\rho S\Sigma J \middle| \hat{R}^{bfn}_y \middle| \Upsilon'\rho' S\Sigma' J \right\rangle = \pm\delta_{\Upsilon\Upsilon'\pm 1}\delta_{\rho\rho'}\delta_{\Sigma\Sigma'}\tfrac{i}{2}\sqrt{J(J+1)-(\Upsilon+\Sigma)(\Upsilon'+\Sigma')}$$
$$+\delta_{\Upsilon\Upsilon'}\delta_{\Sigma\Sigma'}\tfrac{i}{2}\langle\rho S|L_+|\rho' S\rangle - \delta_{\Upsilon\Upsilon'}\delta_{\Sigma\Sigma'}\tfrac{i}{2}\langle\rho S|L_-|\rho' S\rangle \mp \delta_{\Upsilon\Upsilon'\pm 1}\delta_{\Sigma\Sigma'\mp 1}\delta_{\rho\rho'}\tfrac{i}{2}\sqrt{S(S+1)-\Sigma\Sigma'}$$

$$\left\langle \Upsilon\rho S\Sigma J \middle| \hat{R}^{bfn}_z \middle| \Upsilon'\rho' S\Sigma' J \right\rangle = -\delta_{\Upsilon\Upsilon'}\delta_{\Sigma\Sigma'}\left(\Upsilon\delta_{\rho\rho'} - \langle\rho S|L_z|\rho' S\rangle\right).$$

$^1\Sigma^+_u$ state

- Linear:
  - $^1\Sigma^+_u$ big transition moment
  - $^1\Delta_u$ zero transition moment
- Bent
  - mix


C3 Cs bending
Singlets
Triplets
Total Energy (a.u.)
Bending angle (degrees)
-112.9
-113
-113.1
-113.2
-113.3
-113.4
-113.5
-113.6
60
80
100
120
140
160
180
200
220

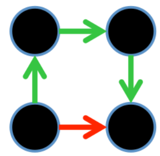
Adiabatic vs. Diabatic

- Unique
- Can change rapidly
- Only KE coupling

- Non-unique
- Does not change rapidly
- Both KE and PE coupling

Diabatization (I)

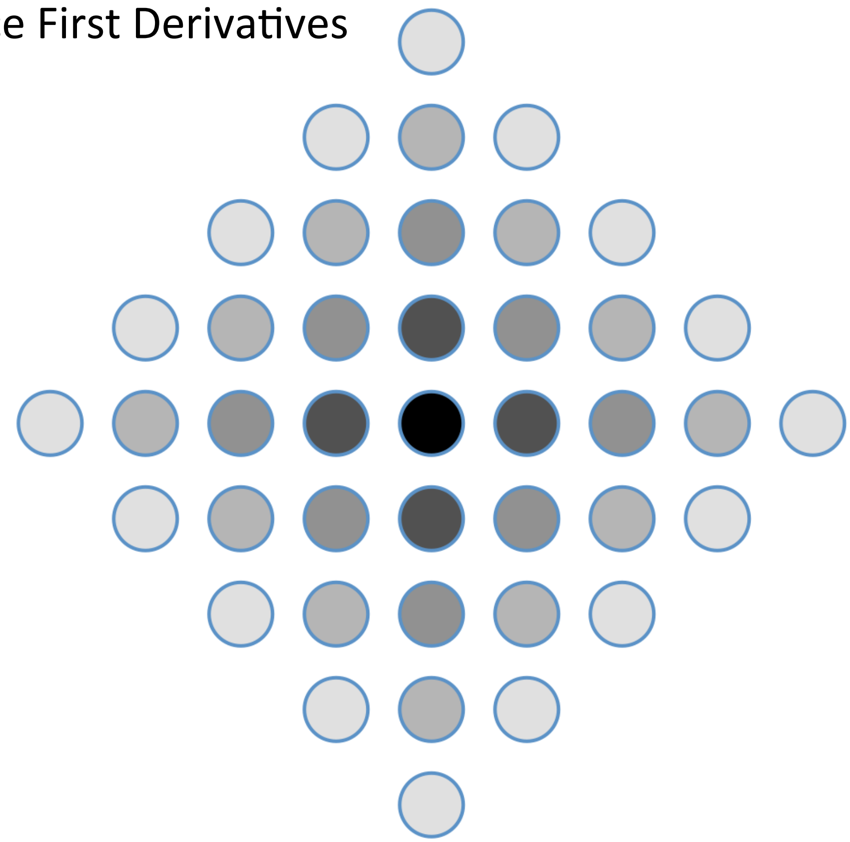
$$\int_a^b \left\langle \psi_n \middle| \nabla_\rho \psi_m \right\rangle d\rho = 0$$



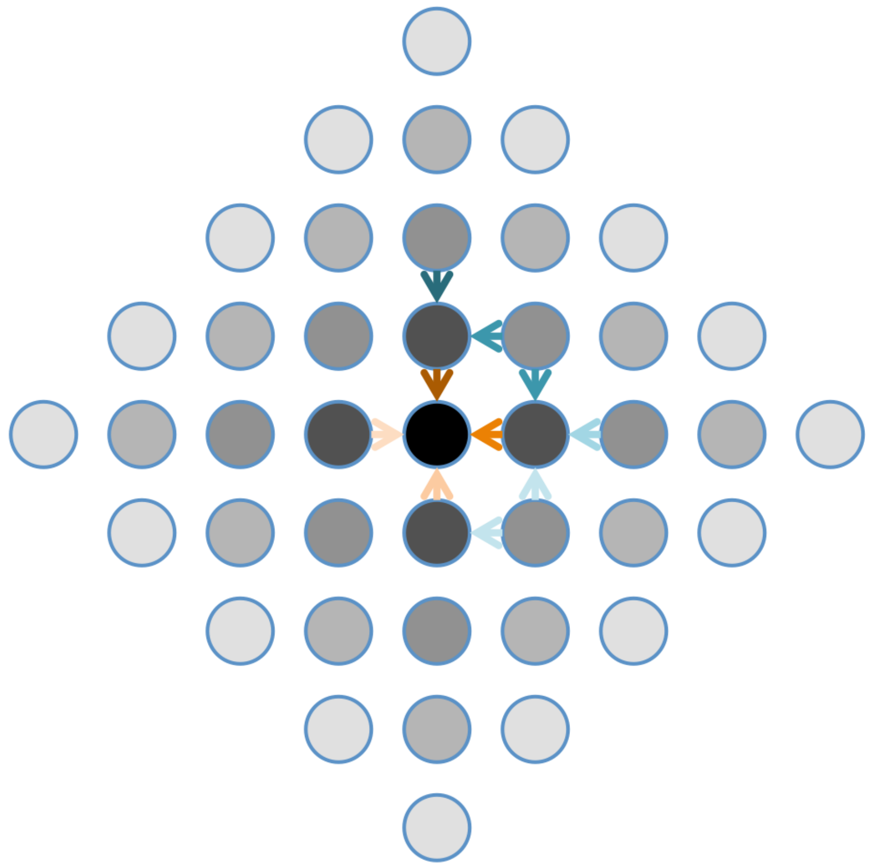
$$\text{minimize } \phi = \left\langle \psi_n^{(\tau)} \middle| \psi_m^{(\tau+d\tau)} \right\rangle^2 + \left\langle \psi_m^{(\tau)} \middle| \psi_n^{(\tau+d\tau)} \right\rangle^2$$

Diabatization (II)

Central Difference First Derivatives



Diabatization (III)



Conclusions

- Good ground state PES
- Have ingredients for coordinate independent Renner-Teller
- Good method to determine diabatic states for polyatomics