Rydberg Anions, Solvated-Electron Precursors and their Dyson Orbitals

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Current Topics in Theoretical Chemistry
Universidad San Francisco de Quito
Cumbayá, Quito, Ecuador
4 July 2019
90th anniversary 🇪🇨 → 🇺🇸

Acknowledgments

- Sponsors: NSF, DTRA
- Auburn Group:
  H. Hernández Corzo
  M. Díaz Tinoco
  F. Pawłowski
- Collaborators:
  E. Miliordos, Auburn
  Gaussian, Inc.
- Hosts: CTTC Organizers, USFQ & Ecuador
- Estudiantes - estoy disponible para contestar *todas* sus preguntas durante o después de esta charla

Quantum Chemistry's Missions

- **Deductive agenda:**

  Deduce properties of molecules from quantum mechanics

  Calculate chemical data, especially if experiments are difficult or expensive

- **Inductive agenda:**

  Identify and explain patterns in structure, spectra, energetics, reactivity

  Deepen and generalize the principles of chemical bonding

E. Schrödinger

G. N. Lewis
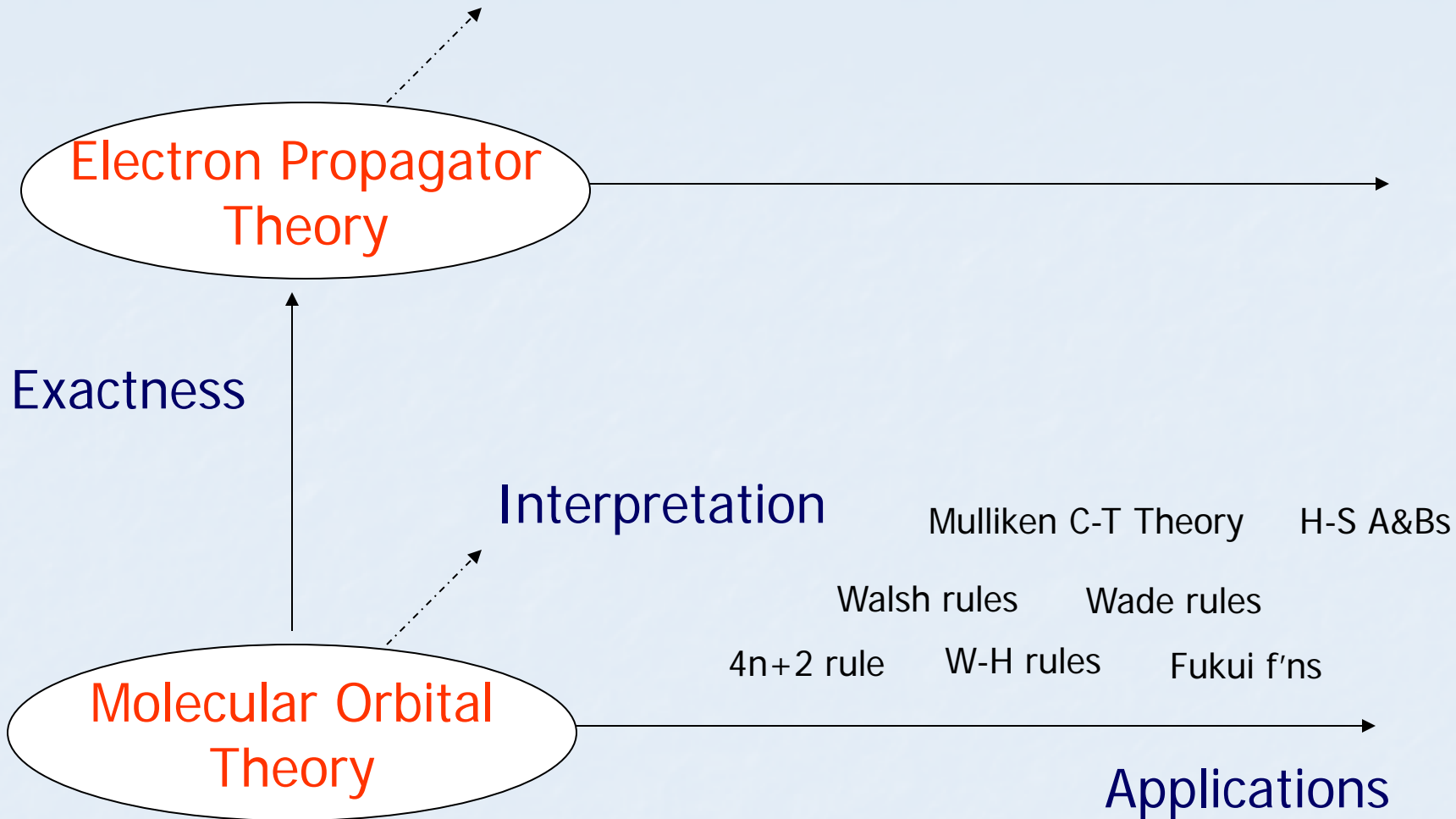
Ψ – Calculation versus Insight

Erwin with his Psi can do
calculations – quite a few.
But one thing has not been seen:
just what does Psi really mean?

Psi remains not rightly understood

Simplified, molecular orbital
concepts continue to inform
chemical reasoning….

E. Hückel
translation: F. Bloch

Electron Propagator
Theory

Exactness

Interpretation

Mulliken C-T Theory   H-S A&Bs

Walsh rules   Wade rules

4n+2 rule   W-H rules   Fukui f'ns

Molecular Orbital
Theory

Applications

One-electron Concepts

- Can an exact theory retain molecular orbital concepts?

- Does electron propagator theory offer a solution to Mulliken's dilemma?

The more accurate the calculations become, the more the concepts vanish into thin air.
- R. S. Mulliken

One-electron Equations

- **Hartree Fock Theory**

  Hartree Fock Equations:

  $$(T_{kin} + U_{nucl} + J_{Coul} - K_{exch})\varphi_i^{HF} \equiv$$

  $$F \, \varphi_i^{HF} = \varepsilon_i^{HF} \, \varphi_i^{HF}$$

  Same operator for all i:
  core, valence, occupied, virtual.

  ε_i^{HF} includes Coulomb and exchange contributions to IEs and EAs

- **Electron Propagator Theory**

  Dyson Equation:

  $$[F + \Sigma(\varepsilon_i^{Dyson})]\varphi_i^{Dyson} = \varepsilon_i^{Dyson} \, \varphi_i^{Dyson}$$

  Self energy, $\Sigma(E)$: Energy dependent, nonlocal operator that varies for each electron binding energy

  ε_i^{Dyson} includes Coulomb, exchange, relaxation and correlation contributions to IEs and EAs

  φ_i^{Dyson} describes effect of electron detachment or attachment on electronic structure

Dyson Orbitals
(Feynman-Dyson Amplitudes)

- Electron Detachment (IEs)

$$\varphi_i^{Dyson}(x_1) =$$
$$N^{-\frac{1}{2}}\int \Psi_N(x_1,x_2,x_3,\ldots,x_N)\Psi^*_{i,N-1}(x_2,x_3,x_4,\ldots,x_N)$$
$$dx_2 dx_3 dx_4 \ldots dx_N$$

- Electron Attachment (EAs)

$$\varphi_i^{Dyson}(x_1) =$$
$$(N+1)^{-\frac{1}{2}}\int \Psi_{i,N+1}(x_1,x_2,x_3,\ldots,x_{N+1})\Psi^*_N(x_2,x_3,x_4,\ldots,x_{N+1})$$
$$dx_2 dx_3 dx_4 \ldots dx_{N+1}$$

Pole Strengths

- Pole strength – criterion of correlation

$$P_i = \int |\varphi_i^{Dyson}(x)|^2 dx$$

$$0 \leq P_i \leq 1$$

- Sudden approximation:

Transition probabilities (intensities) proportional to pole strengths

Orbital Descriptions of Ground States

- ## Hartree-Fock Theory

  Dirac Density Matrix:

  $$\rho(x,x') =$$
  $$\sum_i^{occ.} \varphi_i^{HF}(x)[\varphi_i^{HF}(x')]^*$$

  Total Energy:

  $$E = \tfrac{1}{2}\sum_i^{occ.} (T_{ii} + U_{ii} + \varepsilon_i^{HF})$$

- ## Electron Propagator Theory

  Correlated Density Matrix

  $$\rho(x,x') =$$
  $$\sum_i^{IEs} \varphi_i^{Dyson}(x)[\varphi_i^{Dyson}(x')]^*$$

  Correlated Total Energy:

  $$E = \tfrac{1}{2}\sum_i^{IEs} p_i(T_{ii} + U_{ii} + \varepsilon_i^{Dyson})$$

Electron Propagator Concepts

Electron Correlation

Canonical MO $\longrightarrow$ Dyson Orbital

Orbital Energy $\longrightarrow$ Correlated Electron Binding Energy

Occupation Numbers of 1 or 0 $\longrightarrow$ Intensity Factors Between 1 & 0

Independent-Particle Potential $\longrightarrow$ Energy-dependent, Self-Energy
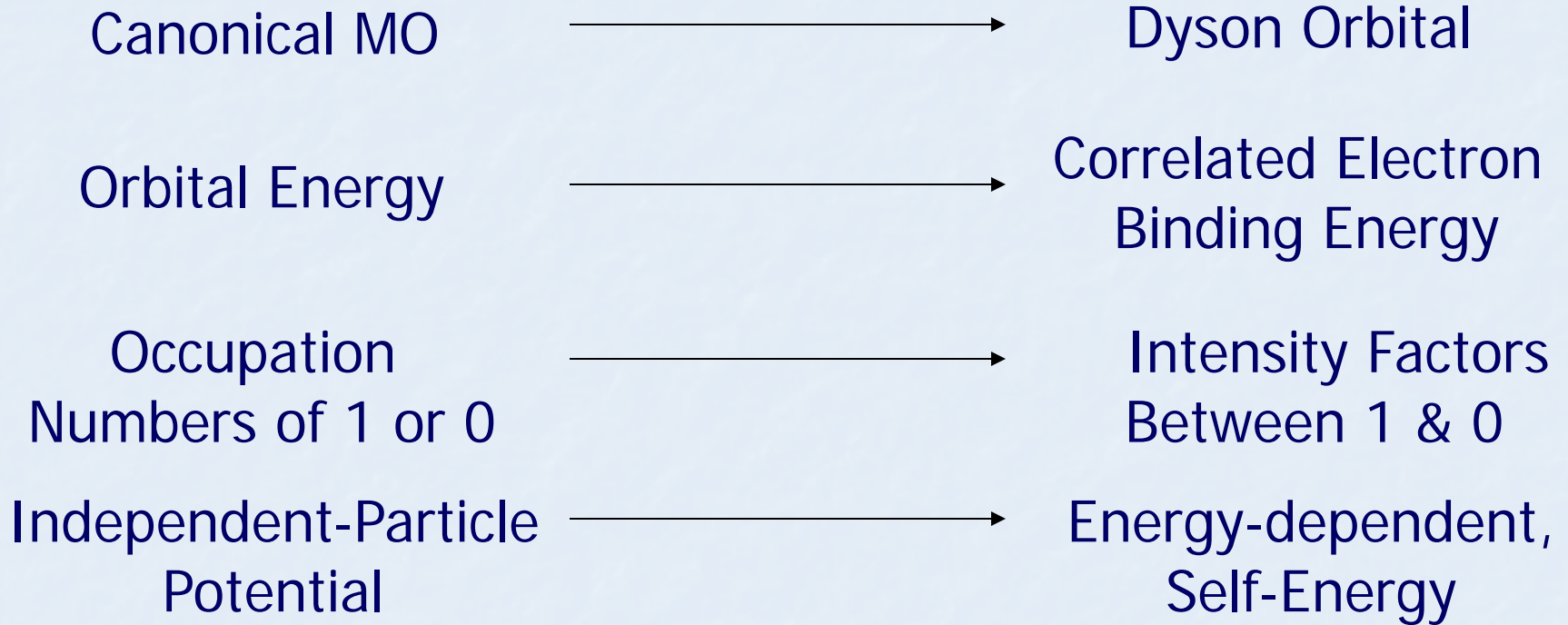
Chemical Reactivity: Superacids & Superhalogens

- *What is the strongest Brønsted-Lowry acid, HB?*

- $HB_n \rightarrow H^+ + B_n^-$ $\Delta E_{n,ion}$ (acidity)

- $HB_n \rightarrow H + B_n$ $\Delta E_{n,cov}$

- *Assume* $\Delta[\Delta E_{cov}] = \Delta E_{n,cov} - \Delta E_{n',cov} \approx 0$

- Hess's Law $\rightarrow$ relative acidities correlate with B electron affinities

$$\Delta[\Delta E_{ion}] \approx \Delta[EA(B)]$$

Champion Superacids & Their Conjugate Bases: Icosahedral $H[HCB_{11}X_{11}]$ & $HCB_{11}X_{11}^-$

X=H
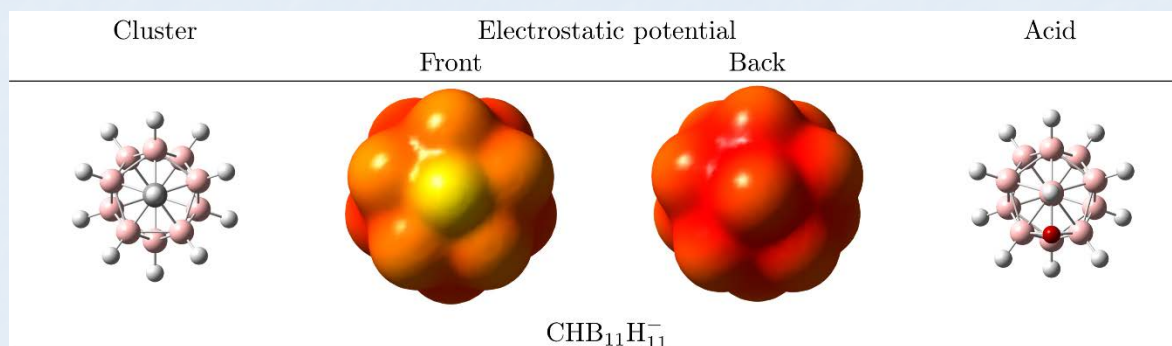
X=F
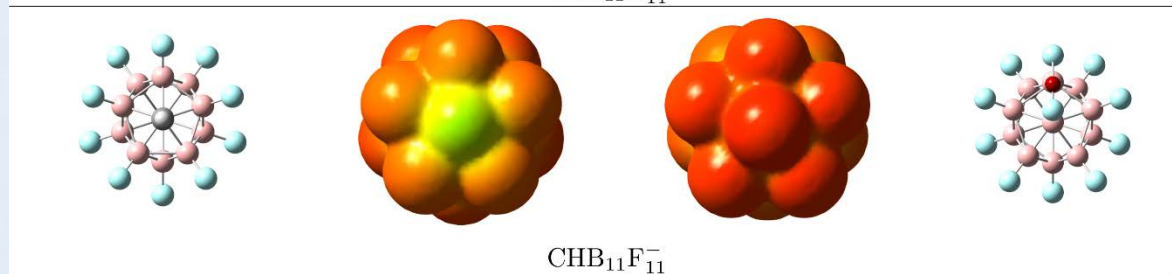
X=Cl
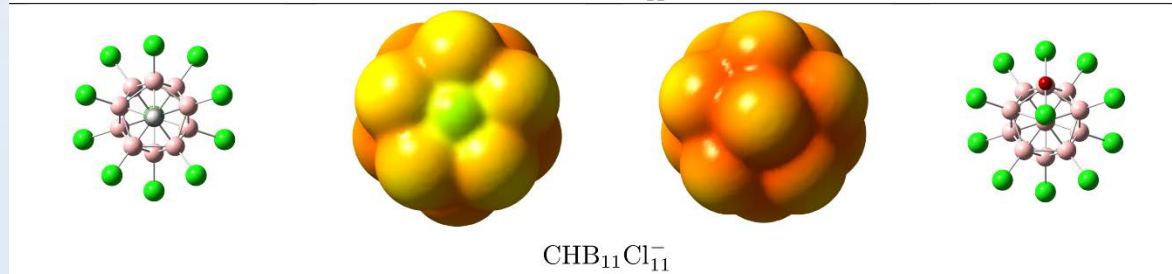
Superacid Champions: Icosahedral Carboranes H[CHB$_{11}$X$_{11}$]

- X = H, F or Cl

- All conjugate bases are superhalides.

- Superacid H$^+$ detaches from BX vertex *opposite* CH.

- ΔE_{ionic} correlates *with 2nd, not 1st* vertical e$^-$ detach. energy (VEDE) of conjugate base.
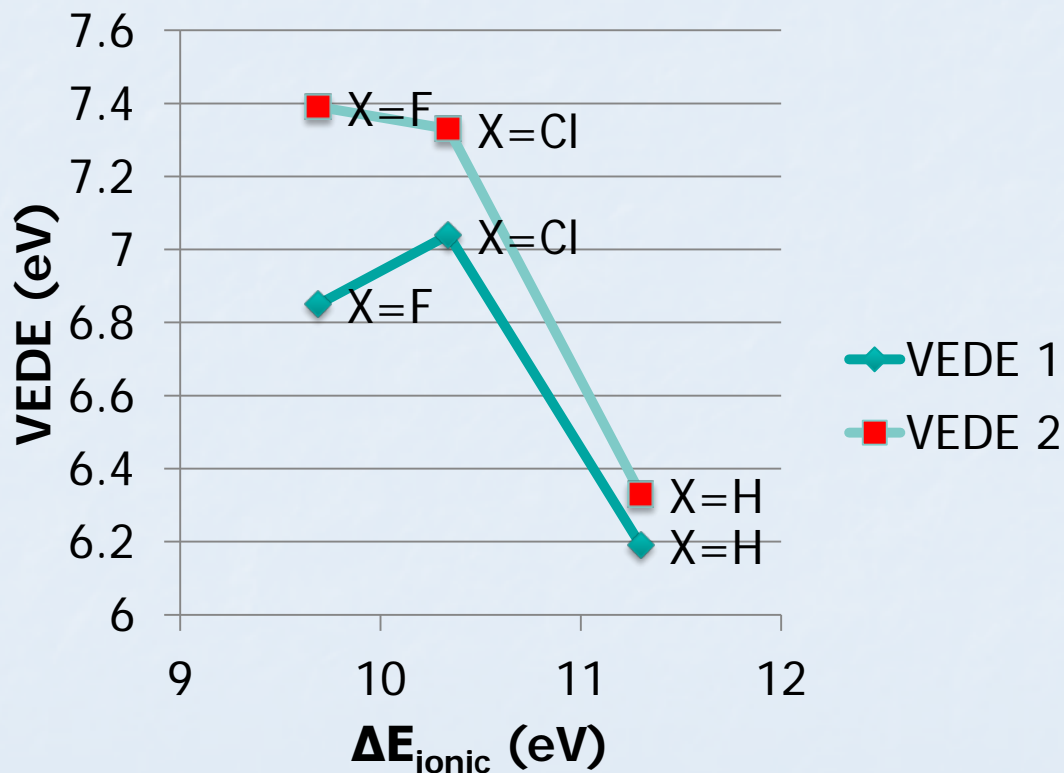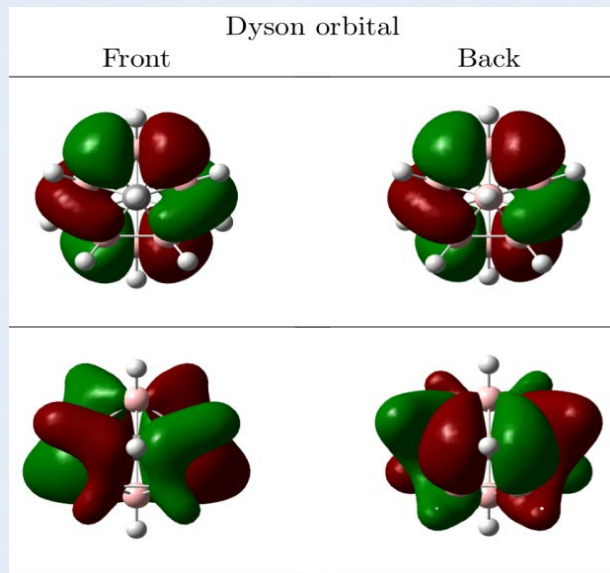
Dyson Orbitals of $CHB_{11}X_{11}^-$ Electron Detachment:

X=H   X=F   X=Cl
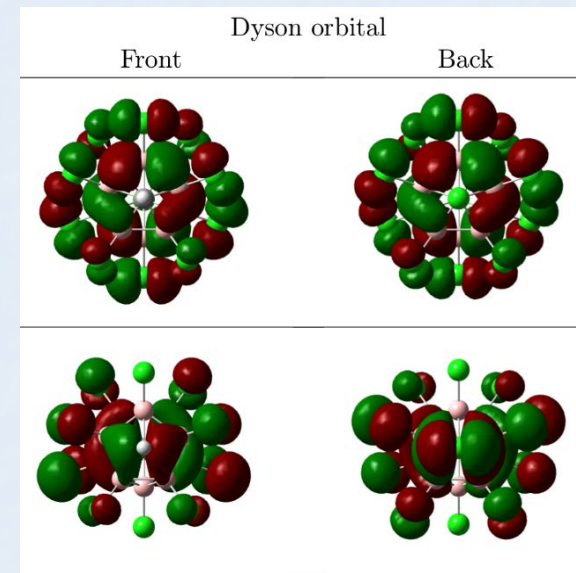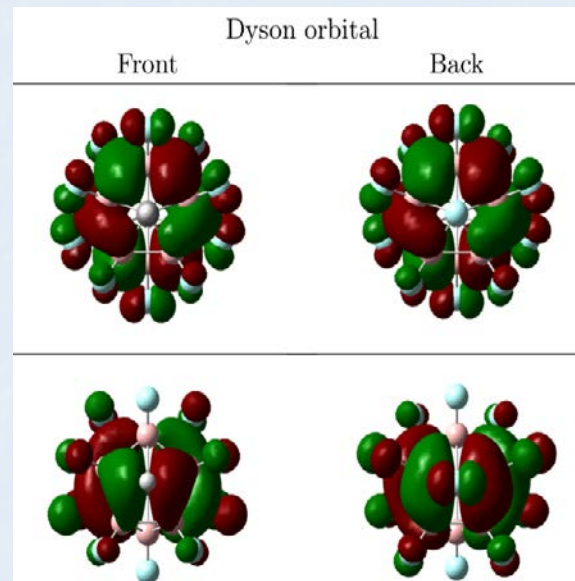
- Agreement with anion PES of L.S. Wang to within 0.1 eV in all cases
- 1st VEDE: front & back views are ≈
- 2nd VEDE: larger lobes on acidic vertex

How to Optimize Superacids

- For $HB_n \rightarrow H + B_n$, $\Delta[\Delta E_{cov}] \approx 0$ is a better approximation for 1st excited state of B_n.

- Therefore, *optimize superacids by maximizing 2nd VEDE of B^- superhalide*, i.e. electron affinity of B excited state

- Excited states can underlie ground-state reactivity.

Approximate Dyson Equations in HF Canonical MO Basis

Diagonal (quasiparticle) self-energies:

D2, P3, P3+, D3, OVGF

$$E = \varepsilon_p + \Sigma_{pp}(E)$$

$$\varphi^{Dyson} = P^{0.5} \, \varphi^{HF}$$

Non-diagonal self-energies:

2ph-TDA, 3+, ADC(3), NR2

$$[\mathbf{F} + \boldsymbol{\Sigma}(E)]\mathbf{C} = \mathbf{C}E$$

$$\varphi^{Dyson} = P^{0.5} \, \Sigma_r \, \varphi_r^{HF} \, C_r$$

Fock and Self-Energy Operators

- Superoperator Metric: $(X|Y) = <0|[X^\dagger,Y]_+|0>$
- Superoperator Hamiltonian: $\hat{H}X = [H,X]_-$

- Primary operator couplings:
$$(a_p^\dagger|\hat{H}a_q^\dagger) = h_{pq} + \Sigma_{rs}<pr||qs>\rho_{rs} = F_{pq}$$

- Secondary operator couplings:
$$\Sigma_{pq}(E)=(a_p^\dagger|\hat{H}\mathbf{f})(\mathbf{f}|E-\hat{H}|\mathbf{f})^{-1}(\mathbf{f}|\hat{H}a_q^\dagger)$$

- Secondary ionization operator manifold:
$$\mathbf{f} = \{\mathbf{f}_3,\mathbf{f}_5,\mathbf{f}_7,...\}$$

Accuracy & Efficiency: Composite EP Methods

- Small anion test set
- Larger anion cases:
  superhalogens
  anion-molecule
  organic rings
  inorganic rings
- Best N^5 diag. method:
  $\Sigma^{P3+}(E) \rightarrow CP3+$
- Best N^5 full method:
  $\Sigma^{NR2}(E) \rightarrow CNR2$
- MUEs ≈ 0.1 eV
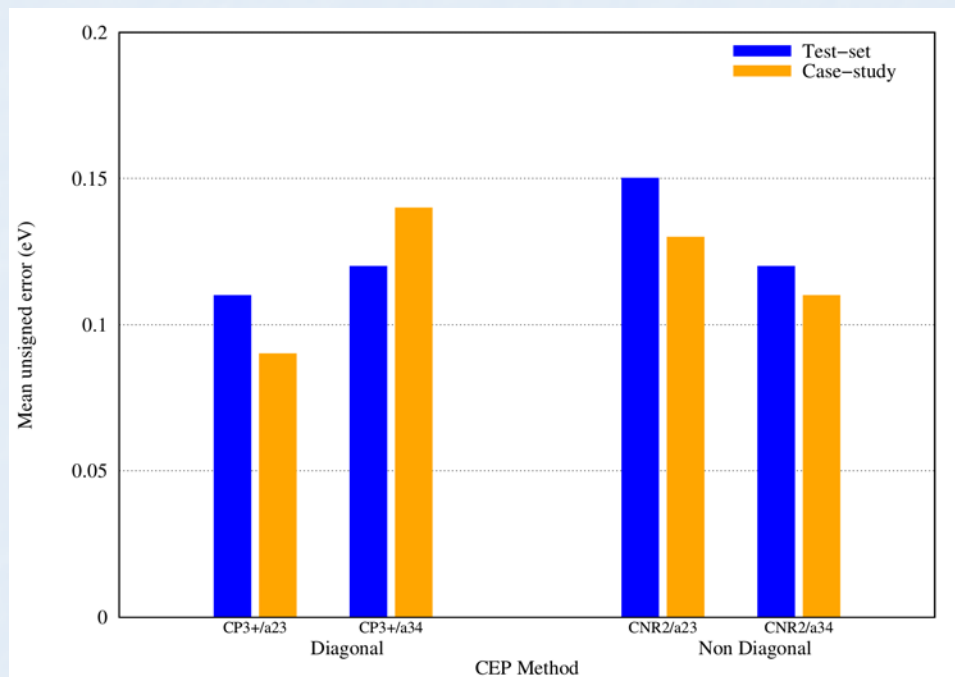
Standard:
extrap. ΔCCSD(T)

Strongly Correlated Reference States: BD-T1 Self-Energy

- Approximate Brueckner determinant & associated t_2 amplitudes in reference state

    - choose BD (Brueckner doubles, coupled-cluster)

- Retain all ring, ladder & mixed ring-ladder $\Sigma(E)$ diagrams

    - F_3 (2hp + 2ph) operator manifold

- Neglect only 2ph-2hp couplings

- Versatility:

    - Valence IEs & EAs

    - Biradicals

    - Core (1s) IEs

Photoelectron Spectrum of NH_4^-

A: H⁻ detachment
with vibrational
excitation of NH_3

X: H⁻(NH_3)
NH_3 increases H⁻ EBE

B: Strange low-EBE peak
Not due to hot NH_4^-
Variable relative intensity
Another isomer of NH_4^-?

Kit Bowen
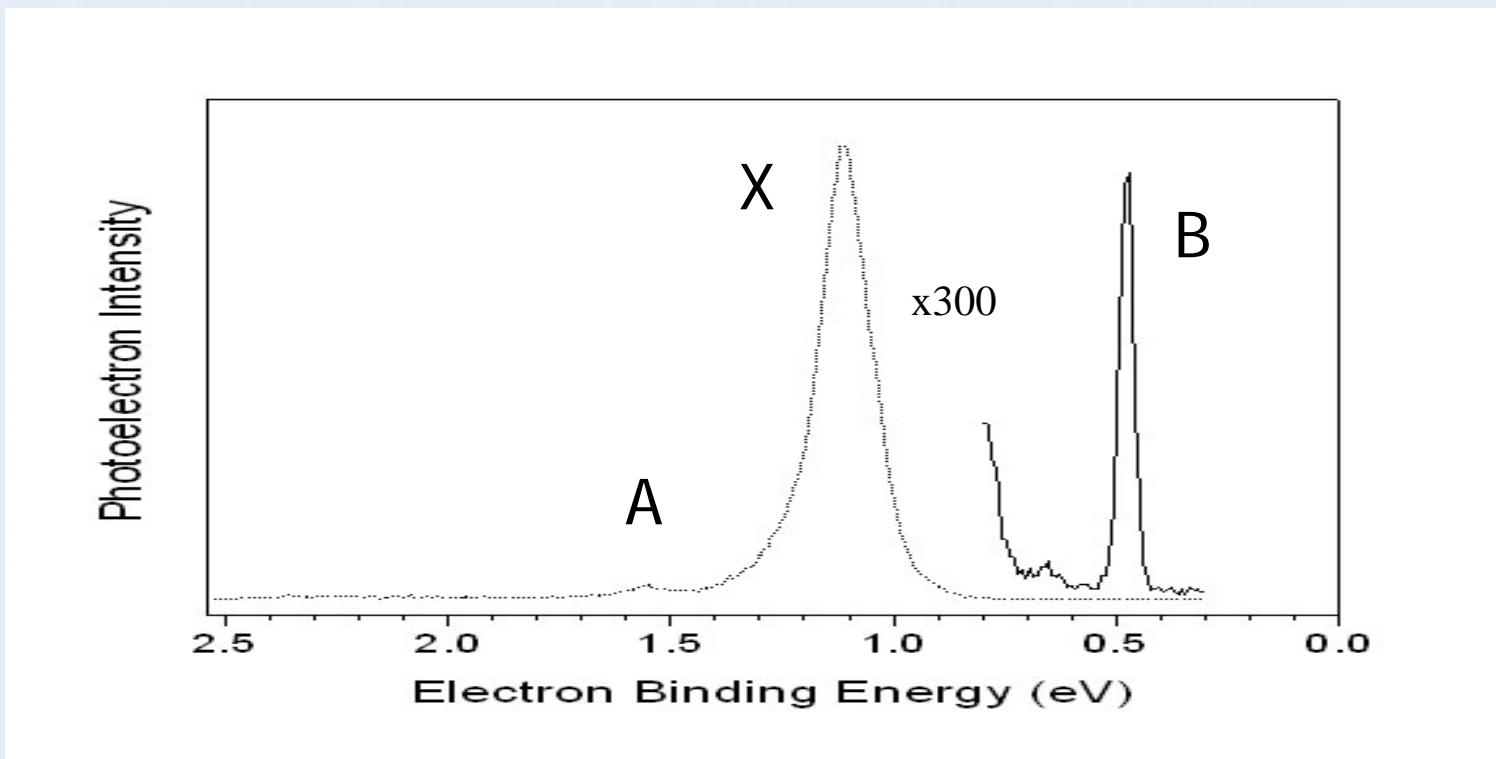
Computational Search: NH_4^- Structures

$H^-(NH_3)$ constituents:

Ammonia molecule: NH_3
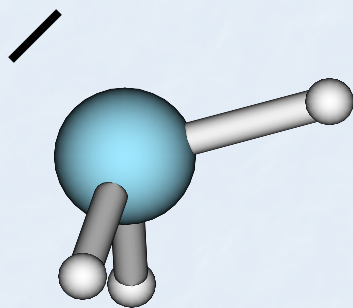
Hydride anion: H^-

Lewis: 3 electron pairs shared in polar NH bonds + 1 unshared pair on N → Partial + charge on H's Partial – charge on N

Anion-molecule structure accounts for dominant peaks

Lewis: 1 electron pair H nucleus has 1+ charge Negative charge attracts + end of polar NH bond

Computational Search:
What is the structure for the low-EBE peak?

Idea: $NH_2^-(H_2)$ anion-molecule complex
Reject: peak would have higher (not lower) EBE

Idea: NH_4^- has 5 valence e^- pairs
Deploy in 4 N-H bonds and 1 unshared pair at the 5 vertices of a trigonal biprism or square pyramid

Calculations find no such structures!
Instead, they spontaneously rearrange ….

….to a heretical structure!

Tetrahedral NH_4^- has 4 equivalent N-H bonds

Defies Lewis theory

Defies valence shell electron pair repulsion theory

Structure similar to that of NH_4^+
So where are the 2 extra electrons?
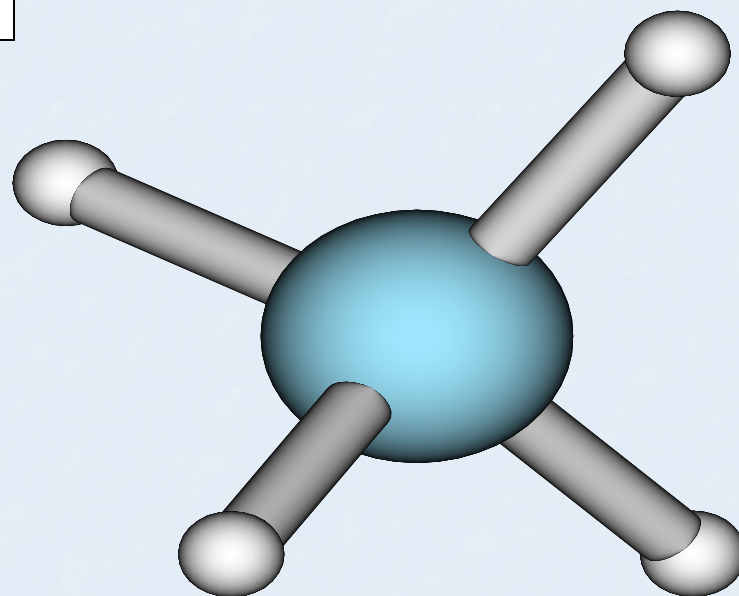
Structural Confirmation: Experiment and Theory

NH$_4^-$ Structure	BD-T1	Experiment
H$^-$(NH$_3$)	1.07	1.11 ± 0.02 eV
Tetrahedron	0.48	0.47 ± 0.02

Predicted EBEs from Electron Propagator Theory for Anion(molecule) and Tetrahedral forms of NH$_4^-$ coincide with peaks from photoelectron spectrum

Dyson Orbitals for EBEs of NH_4^-
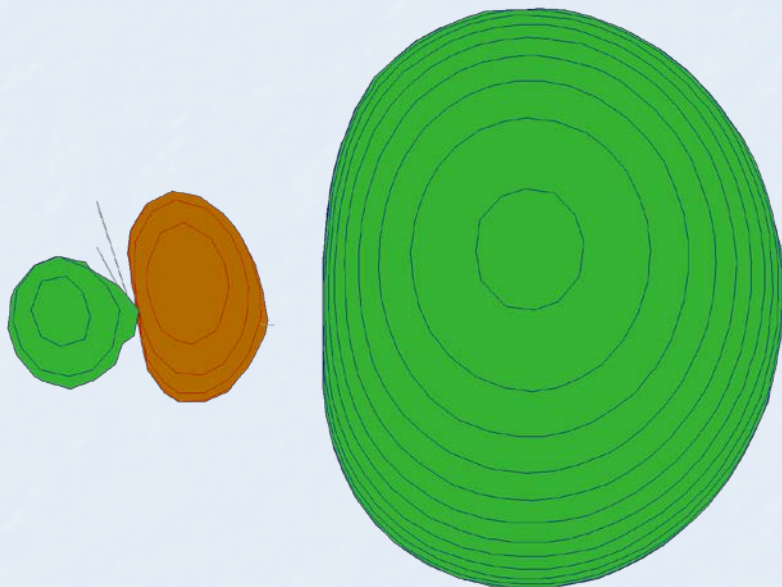
$H^-(NH_3)$ has 2 electrons in hydride-centered orbital with minor N-H delocalization. EBE is 1.07 eV
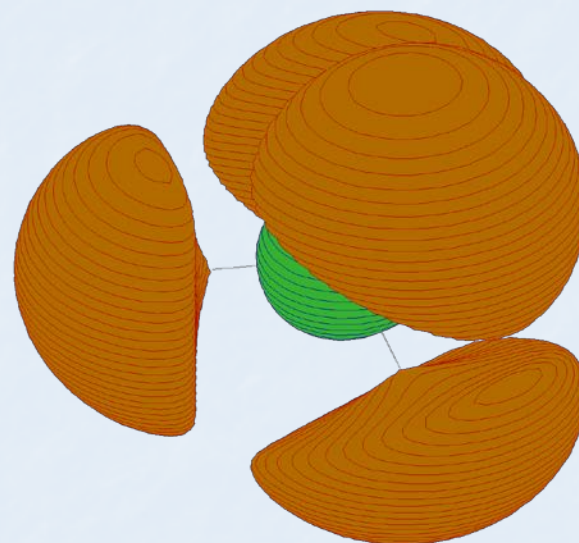
Tetrahedral NH_4^- has 2 diffuse electrons located chiefly outside of NH_4^+ core. EBE is 0.47 eV

Double Rydberg Anions

- Highly correlated motion of two diffuse (Rydberg) electrons in the field of a positive ion (NH_4^+, OH_3^+)

- United atom limit is an alkali anion: Na^-

- Extravalence atomic contributions in Dyson orbitals

NH_4^-

OH_3^-
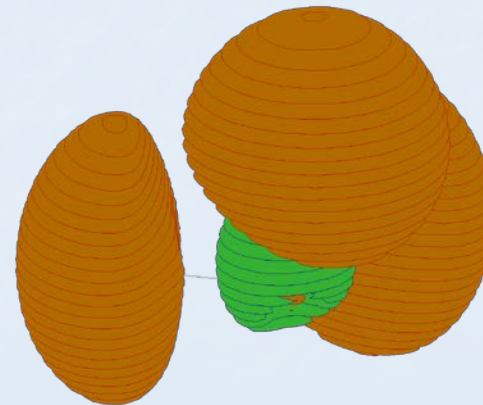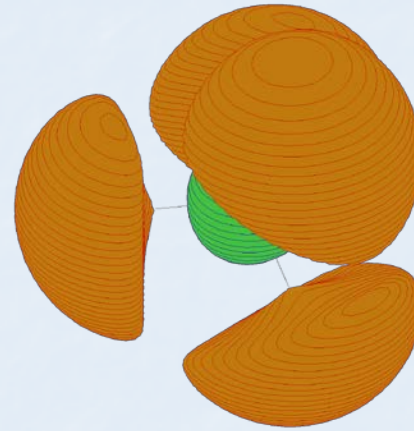
Photoelectron Spectrum of $N_2H_7^-$

X: $H^-(NH_3)_2$ e$^-$ detachment   B & C: two low EBEs!
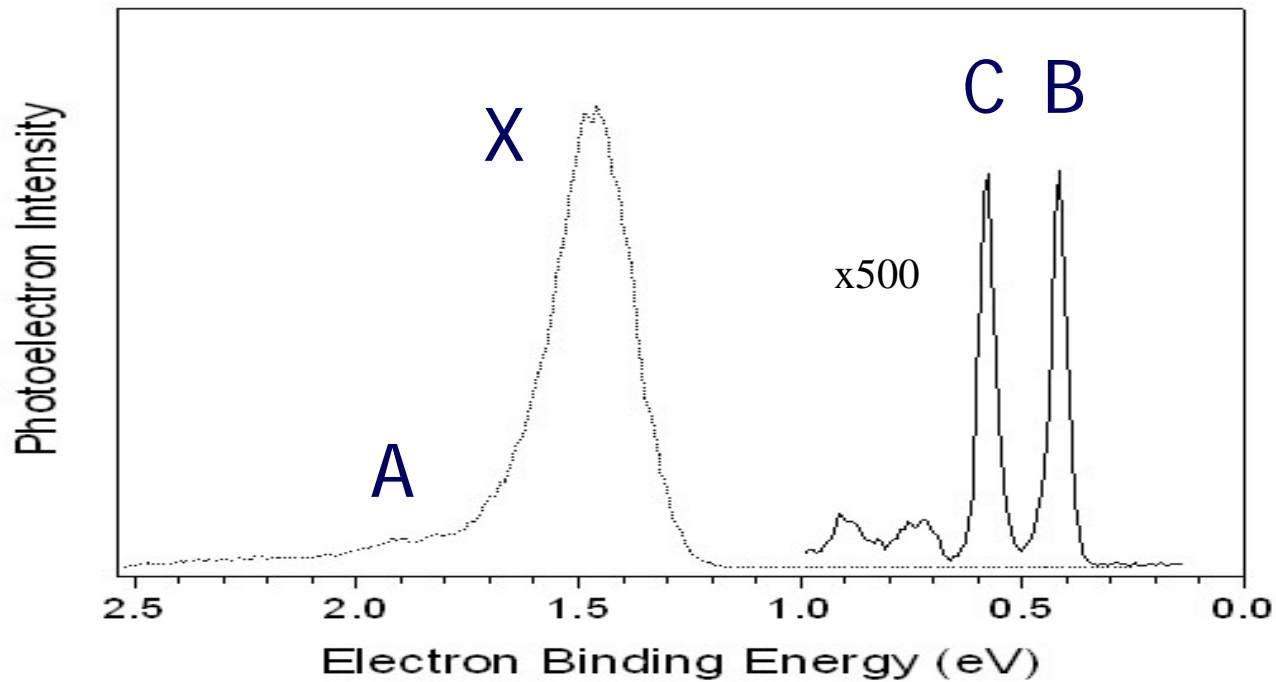
Calculated $N_2H_7^-$ Structures

- $H^-(NH_3)_2$ anion-
  molecule complex
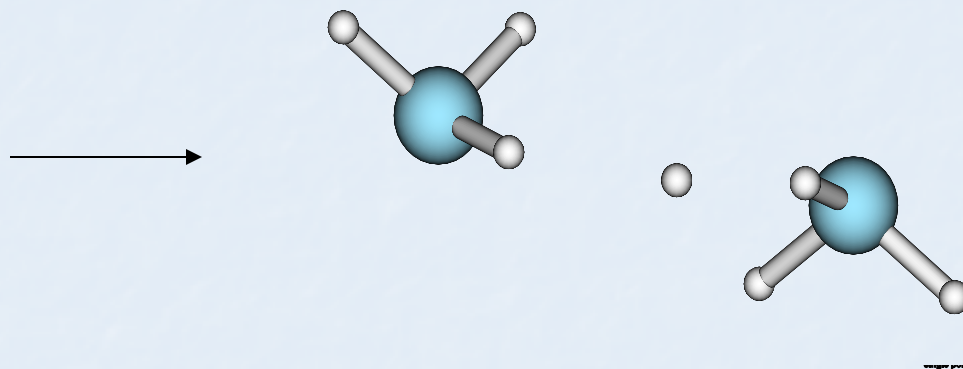
- $NH_4^-(NH_3)$ anion-
  molecule complex
  with tetrahedral NH_4^-
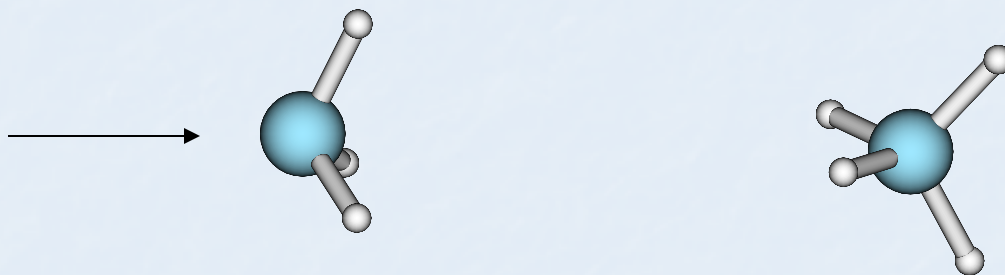
- $N_2H_7^-$ with hydrogen bond
  (similar to $N_2H_7^+$)
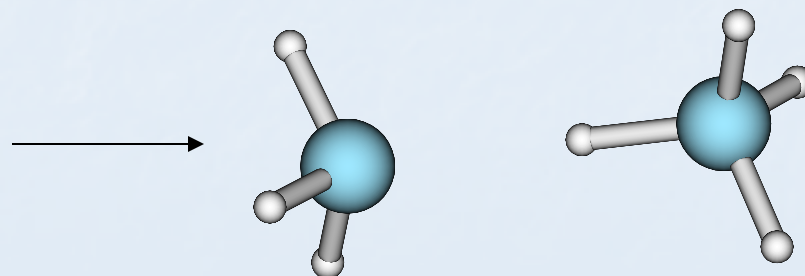
$N_2H_7^-$ EBEs and Dyson Orbitals

$H^-(NH_3)_2$ has hydride centered Dyson orbital
BD-T1 predicts 1.49 eV for EBE
Peak observed in spectrum at 1.46 ± 0.02 eV
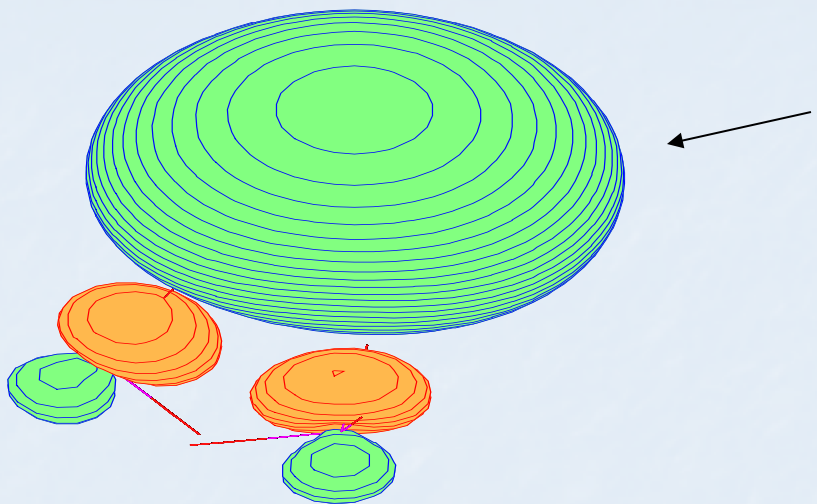
Dyson orbital concentrated near NH_4^-
BD-T1 predicts 0.60 eV for EBE
Peak observed at 0.58 ± 0.02 eV
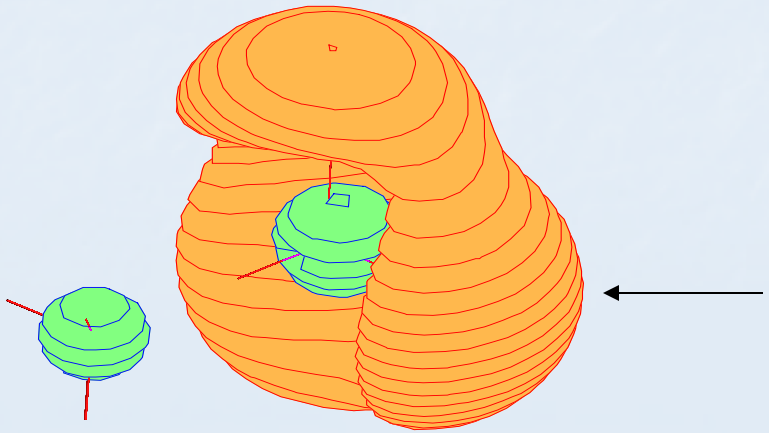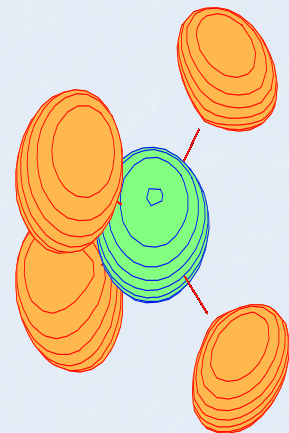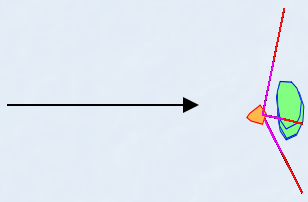
Dyson orbital concentrated near 3 hydrogens
BD-T1 predicts 0.42 eV for EBE
Peak observed at 0.42 ± 0.02 eV

$N_5H_{16}^-$ EBE & Dyson Orbital

- Experiment: **relatively intense**, low-energy peak at 0.43 eV

- EPT EBE = 0.39 eV for T_d DRA's $^2A_1$ final state

- First solvation sphere is complete

- Diffuse a_1 Dyson orbital
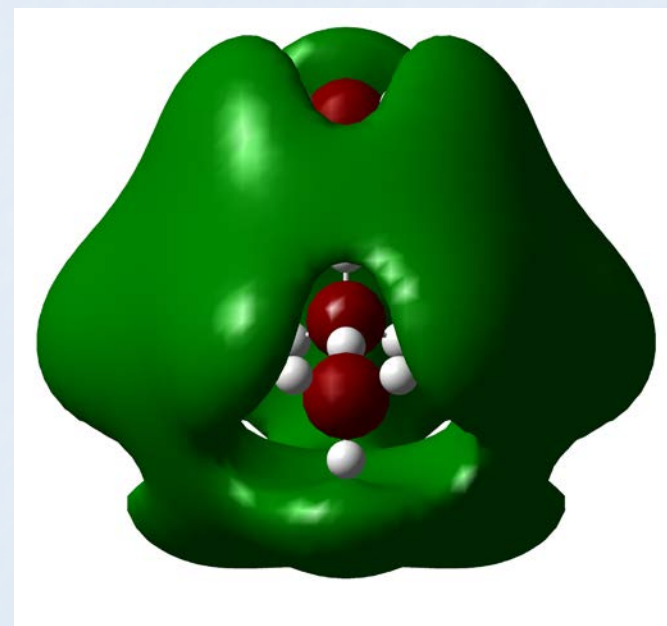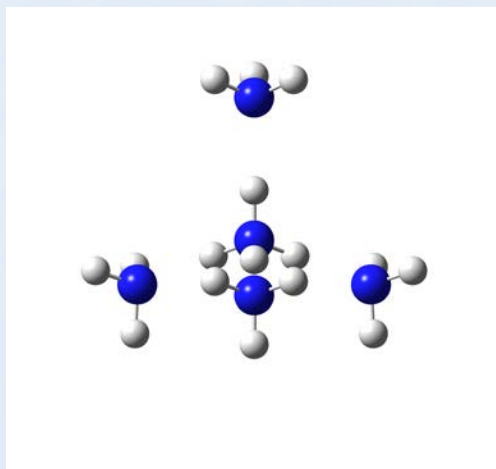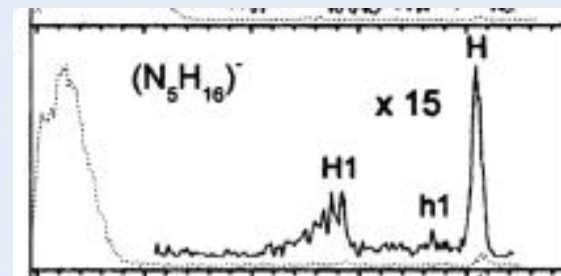
$N_5H_{16}^-$ Shake-up EBE

- Experiment: shake-up peak with 0.70 eV displacement

- EPT shake-up displacement = 0.58 eV for $^2T_2$ final state

- Diffuse a_1 and t_2 Dyson orbitals of e^- attachment to $N_5H_{16}^+$

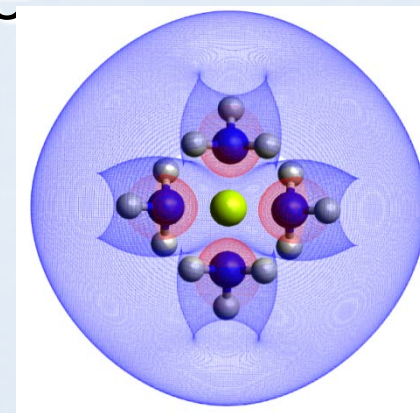- N_5H_{16} Aufbau principle: 1s, 1p, 1d, 2s, 1f, 2p, 2d
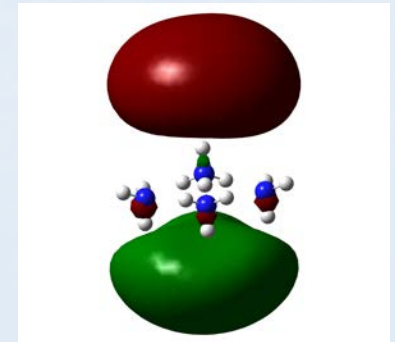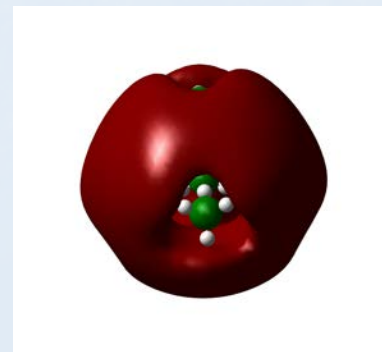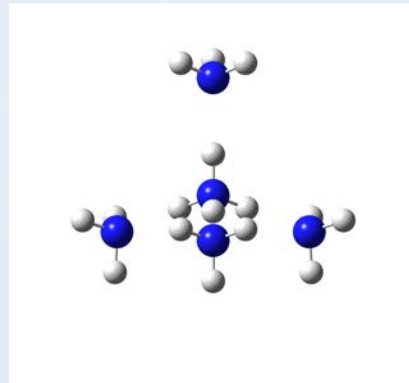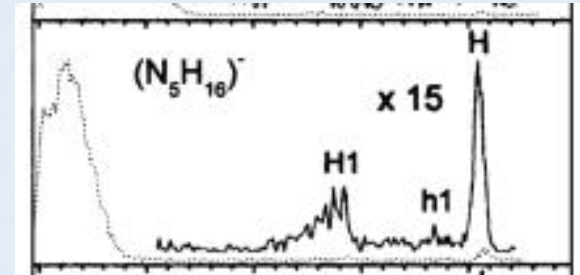
Toward Diffuse Electron Pairs in Condensed Phases

E. Miliordos

- Require charge neutrality – replace central cation by a *dication*

- Could $Be(NH_3)_4$ have two diffuse electrons that surround a T_d $Be(NH_3)_4^{2+}$ core?

- Double Rydberg *Molecule* OR Solvated Electron Precursor

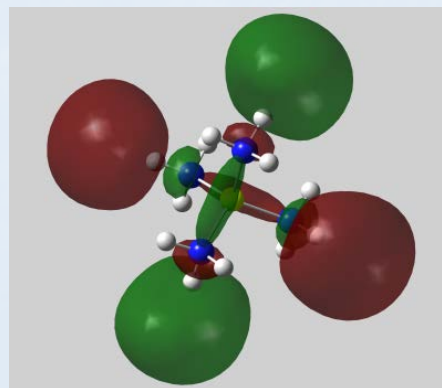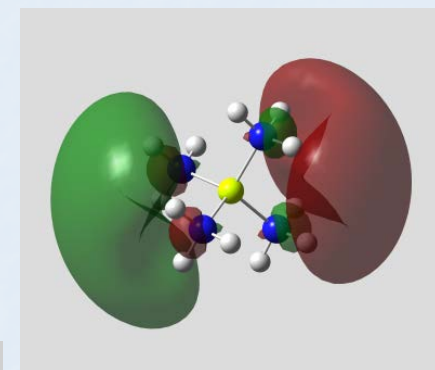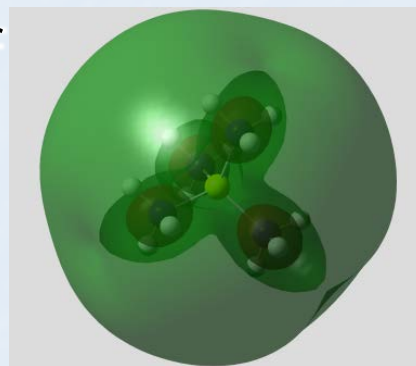# Aufbau Principle for Solvated Electron Precursors

- Dyson orbitals for EAs of $Be(NH_3)_4^{n+}$ (n=1,2) → ground & excited states for n = 0, 1

- Diffuse Aufbau principle:

  1s 1p 1d 2s 1f 2p

- $Be(NH_3)_{16}^{n+}$ has 1g level
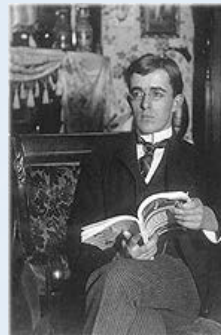

- Paramagnetic cores

- Covalent oligomers

Electron Pair Concepts: Old and New

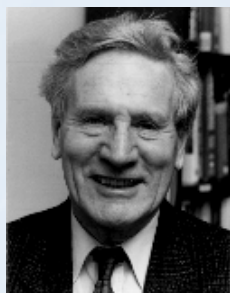Chemical bonds arise from pairs of electrons shared between atoms

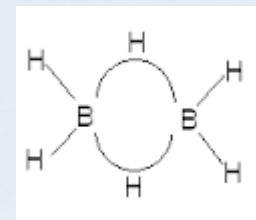G.N. Lewis   I. Langmuir   W.N. Lipscomb

Unshared pairs localized on single atoms affect bond angles

R.J. Gillespie   R.S. Nyholm

Molecular cations may bind a diffuse e⁻ pair: Double Rydberg Anions & Solvated e⁻ Precursors

Insights from Electron Propagator Theory

- *Ab initio* prediction and interpretation of spectra and energetics

- Rigorous, one-electron concepts deepen and generalize qualitative chemical notions