

# *Electronic Structure Theory*

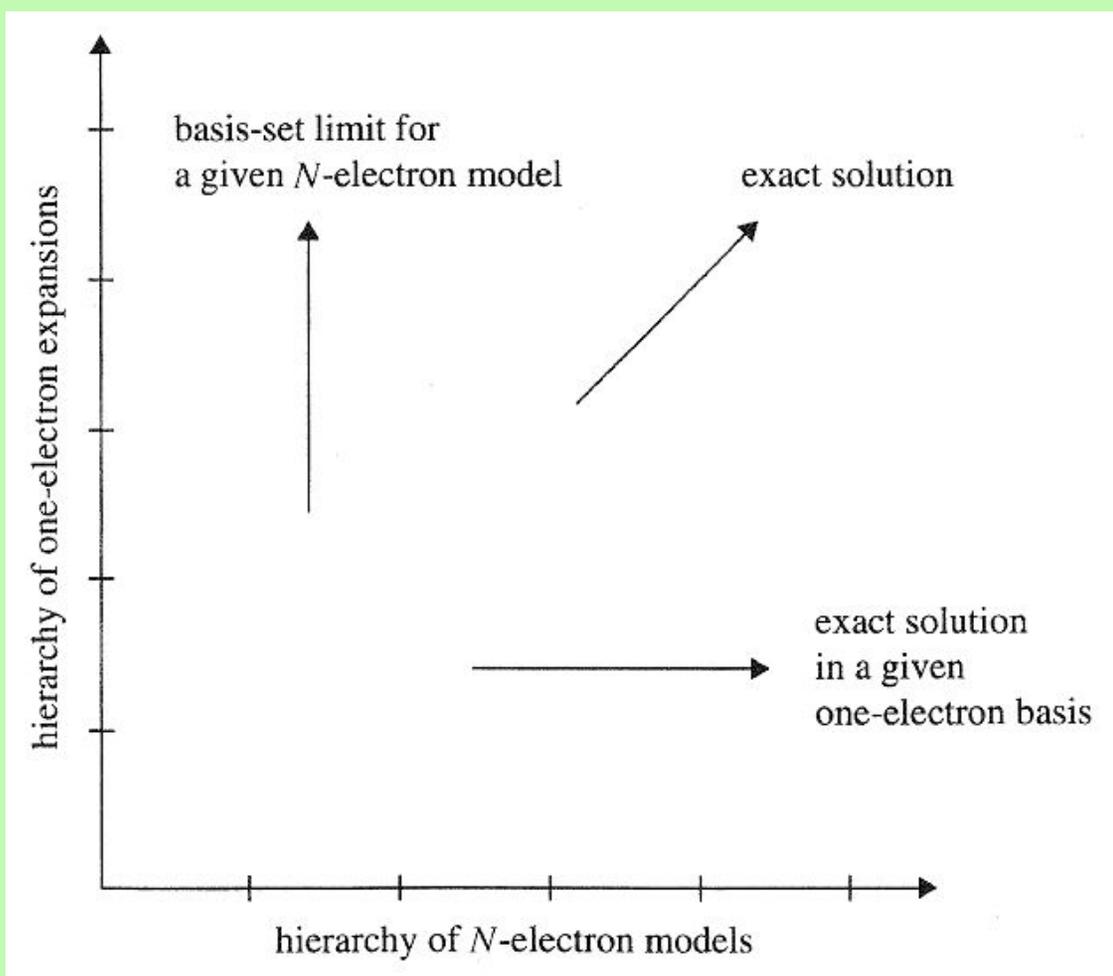
## *TSTC Session 9*



1. Born-Oppenheimer approx.- energy surfaces
2. Mean-field (Hartree-Fock) theory- orbitals
3. Pros and cons of HF- RHF, UHF
4. Beyond HF- why?
5. First, one usually does HF-how?
6. Basis sets and notations
7. MPn, MCSCF, CI, CC, DFT
8. Gradients and Hessians
9. **Special topics: accuracy, metastable states**

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Keeping in mind that there are **two independent directions** (**basis sets** and **method** for treating electron **correlation**), it is useful to look into **how various approaches do** when applied to a **common set of molecules** of various types.



At various times, it will be appropriate to quote **various measures**:

## Measures of errors

$$\Delta_i = R_i^{\text{calc}} - R_i^{\text{exp}}$$

error in individual bond length

$$\bar{\Delta} = \frac{1}{n} \sum_{i=1}^n \Delta_i$$

mean error

$$\Delta_{\text{std}} = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (\Delta_i - \bar{\Delta})^2}$$

standard deviation

$$\Delta_{\text{abs}} = \frac{1}{n} \sum_{i=1}^n |\Delta_i|$$

mean absolute error

$$\Delta_{\text{max}} = \max_i |\Delta_i|$$

maximum error

In the data we display, the following **molecules, bases,** and **methods** were employed:

***19 closed-shell molecules***

CH<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, NH<sub>3</sub>, HF, N<sub>2</sub>, CO, HCN, HNC, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>,  
CH<sub>2</sub>O, HNO, N<sub>2</sub>H<sub>2</sub>, HOF, CO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, F<sub>2</sub>

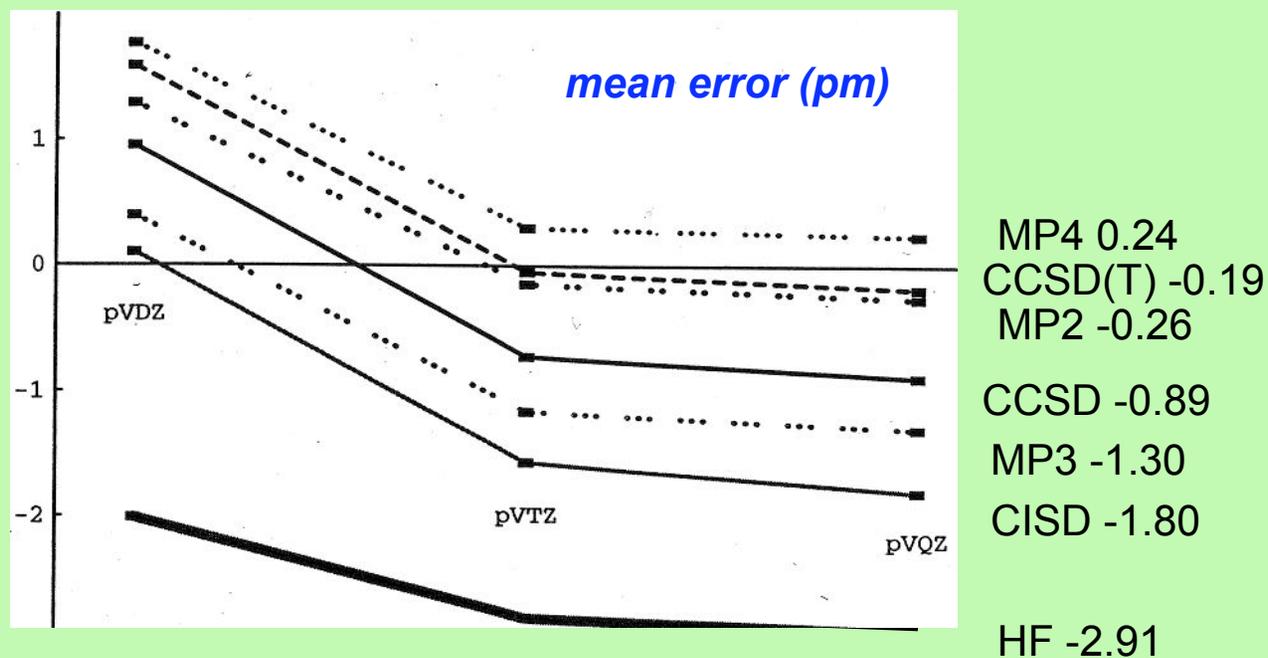
***Wave function methods***

HF, CISD, MP2, MP3, MP4, CCSD, CCSD(T)

***Basis sets***

cc-pVXZ, X=D,T,Q

## How about geometries? Equilibrium bond lengths



*highly systematic behavior !*

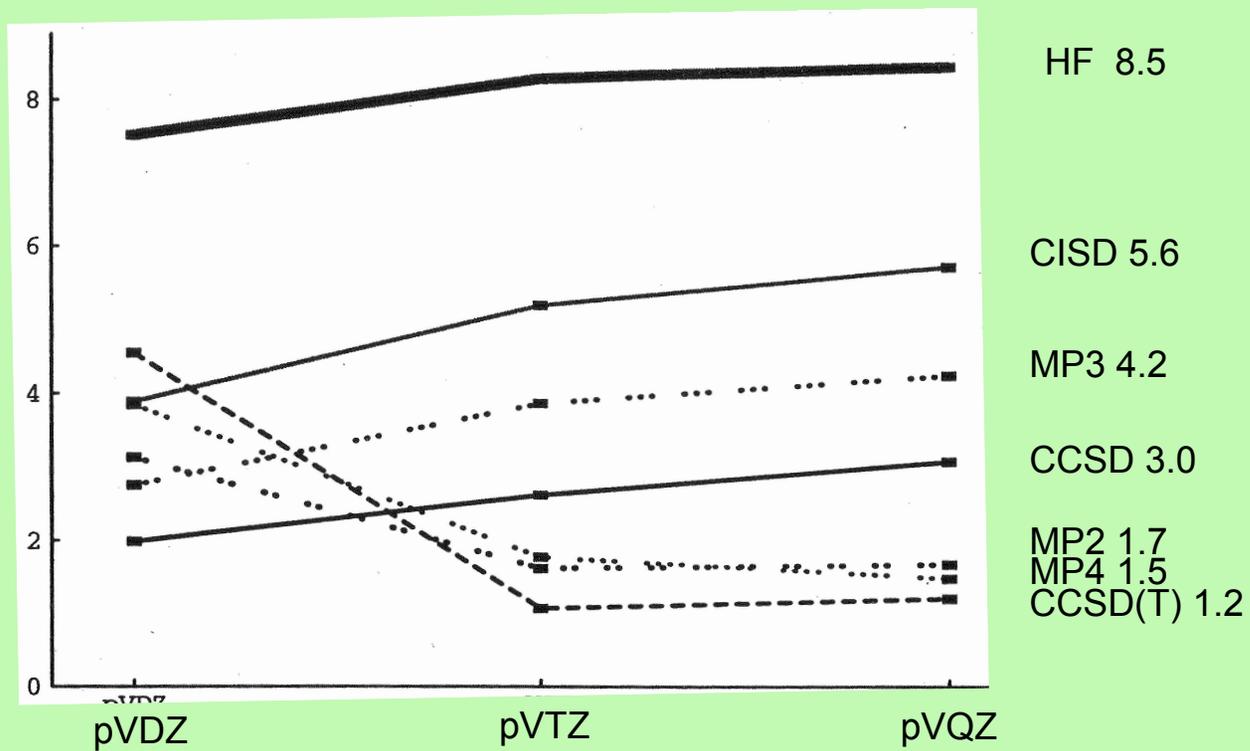
1) *bonds shorten with increasing basis*

DZ > TZ > QZ

2) *bond lengthen with improvements in N-electron model*

$$\underbrace{HF}_{\text{singles}} < \underbrace{CISD < MP3 < CCSD < MP2}_{\text{doubles}} < \underbrace{CCSD(T) < MP4}_{\text{triples}}$$

# Maximum absolute error (pm)

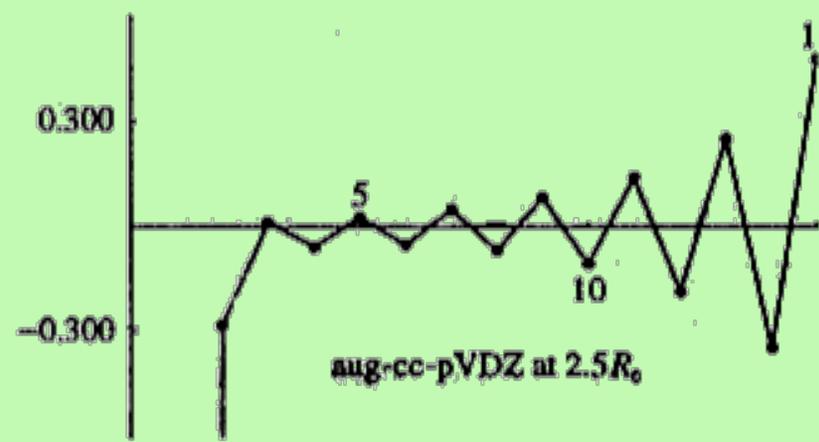
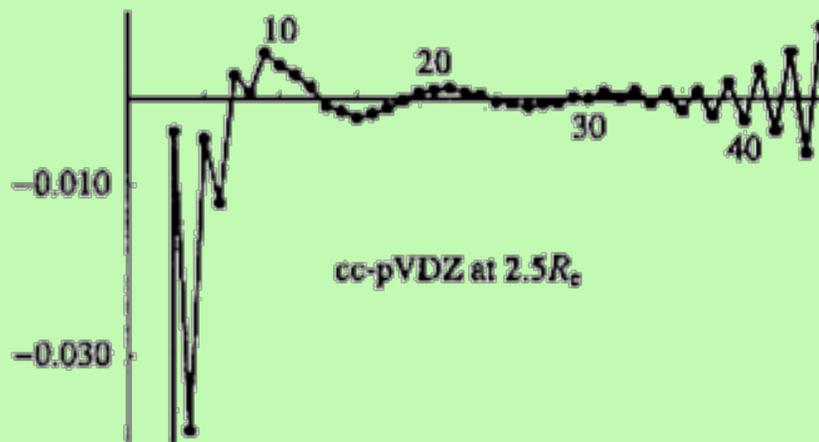
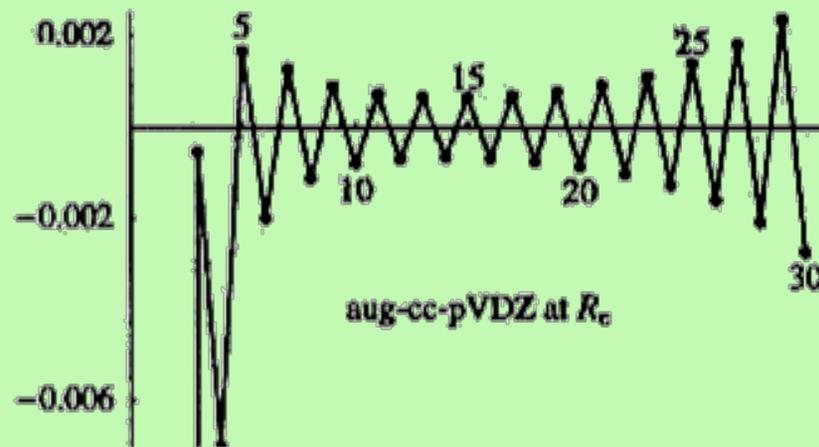
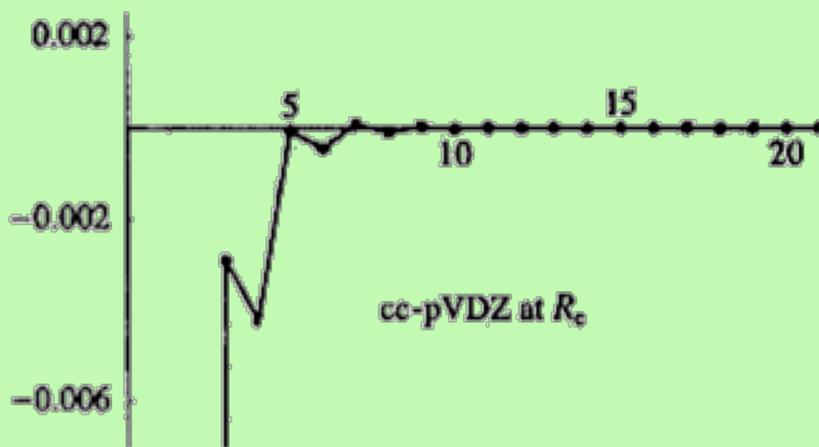


## Bond lengths (pm)

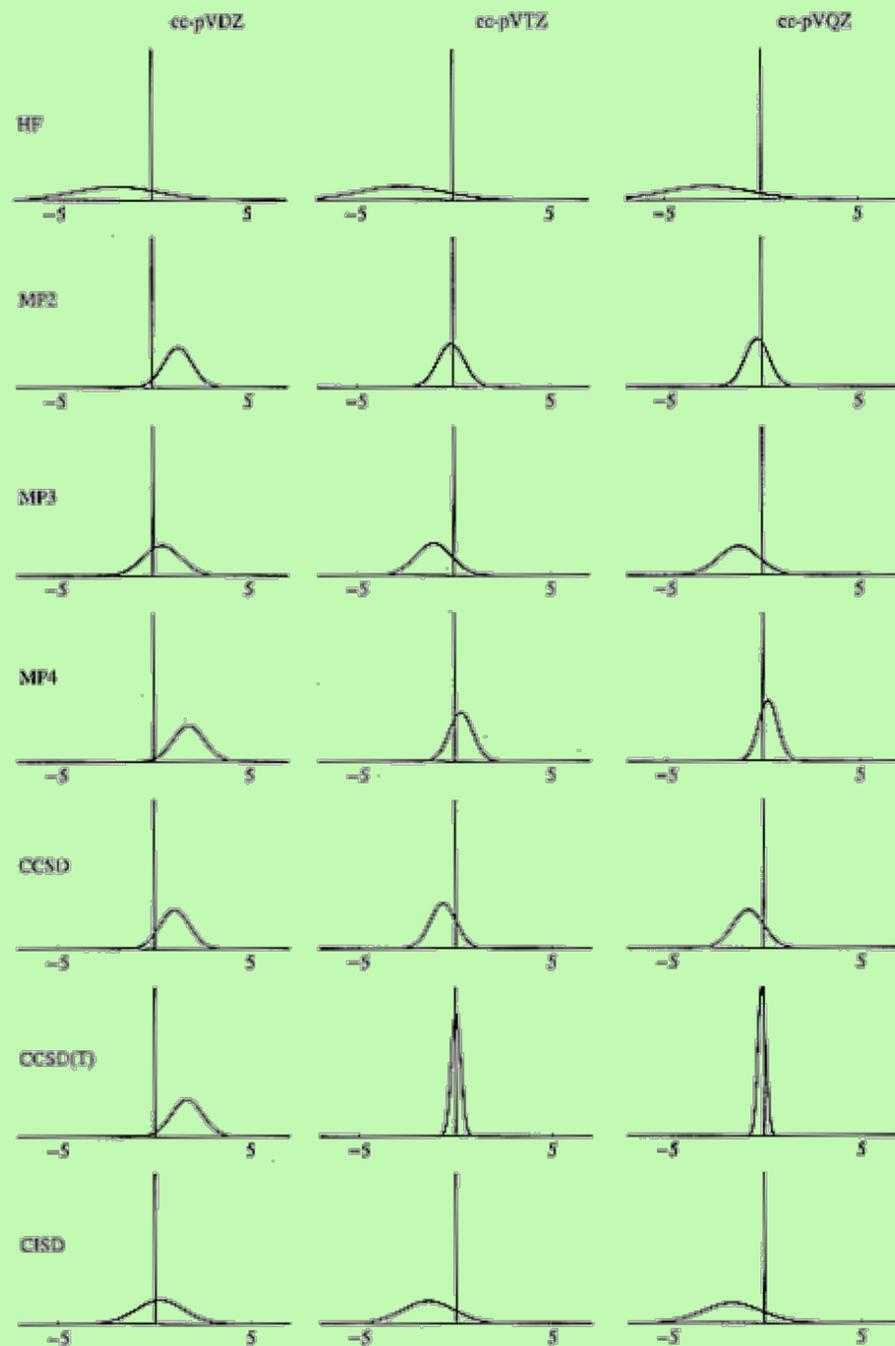
For experimental bond lengths, the number in parentheses is the uncertainty

molekyle	bindingslængde	eksperimentelt	empirisk	CCSD(T)/ cc-pCVQZ
H <sub>2</sub>	R <sub>HH</sub>	74.144	–	74.19
HF	R <sub>FH</sub>	91.680(8)	91.69	91.58
H <sub>2</sub> O	R <sub>OH</sub>	95.72	95.75	95.71
HOF	R <sub>OH</sub>	96.57(16)	96.78	96.57
H <sub>2</sub> O <sub>2</sub>	R <sub>OH</sub>	96.7	–	96.19
HNC	R <sub>NH</sub>	99.40(8)	99.49	99.53
NH <sub>3</sub>	R <sub>NH</sub>	101.1(6)	101.16	101.12
N <sub>2</sub> H <sub>2</sub>	R <sub>NH</sub>	102.9(1)	102.86	102.84
HNO	R <sub>NH</sub>	<b>106.3</b>	105.17	105.24
C <sub>2</sub> H <sub>2</sub>	R <sub>CH</sub>	106.215(17)	106.13	106.21
HCN	R <sub>CH</sub>	106.501(8)	106.53	106.55
C <sub>2</sub> H <sub>4</sub>	R <sub>CH</sub>	108.1(2)	108.07	108.09
CH <sub>4</sub>	R <sub>CH</sub>	108.58(10)	108.59	108.64
N <sub>2</sub>	R <sub>NN</sub>	109.768(5)	109.77	109.81
CH <sub>2</sub> O	R <sub>CH</sub>	110.05(20)	110.07	110.08
CH <sub>2</sub>	R <sub>CH</sub>	110.7(2)	110.63	110.68
CO	R <sub>CO</sub>	112.832	112.84	112.89
HCN	R <sub>CN</sub>	115.324(2)	115.34	115.38
CO <sub>2</sub>	R <sub>CO</sub>	115.995	116.01	116.04
HNC	R <sub>CN</sub>	116.89(2)	116.87	116.93
C <sub>2</sub> H <sub>2</sub>	R <sub>CC</sub>	120.257(9)	120.37	120.37
CH <sub>2</sub> O	R <sub>CO</sub>	120.33(10)	120.47	120.43
HNO	R <sub>NO</sub>	<b>121.2</b>	120.86	120.85
N <sub>2</sub> H <sub>2</sub>	R <sub>NN</sub>	124.7(1)	124.57	124.67
C <sub>2</sub> H <sub>4</sub>	R <sub>CC</sub>	133.4(2)	133.07	133.12
F <sub>2</sub>	R <sub>FF</sub>	141.193	141.24	141.13
HOF	R <sub>FO</sub>	143.50(31)	143.44	143.26
H <sub>2</sub> O <sub>2</sub>	R <sub>OO</sub>	145.56	–	144.97

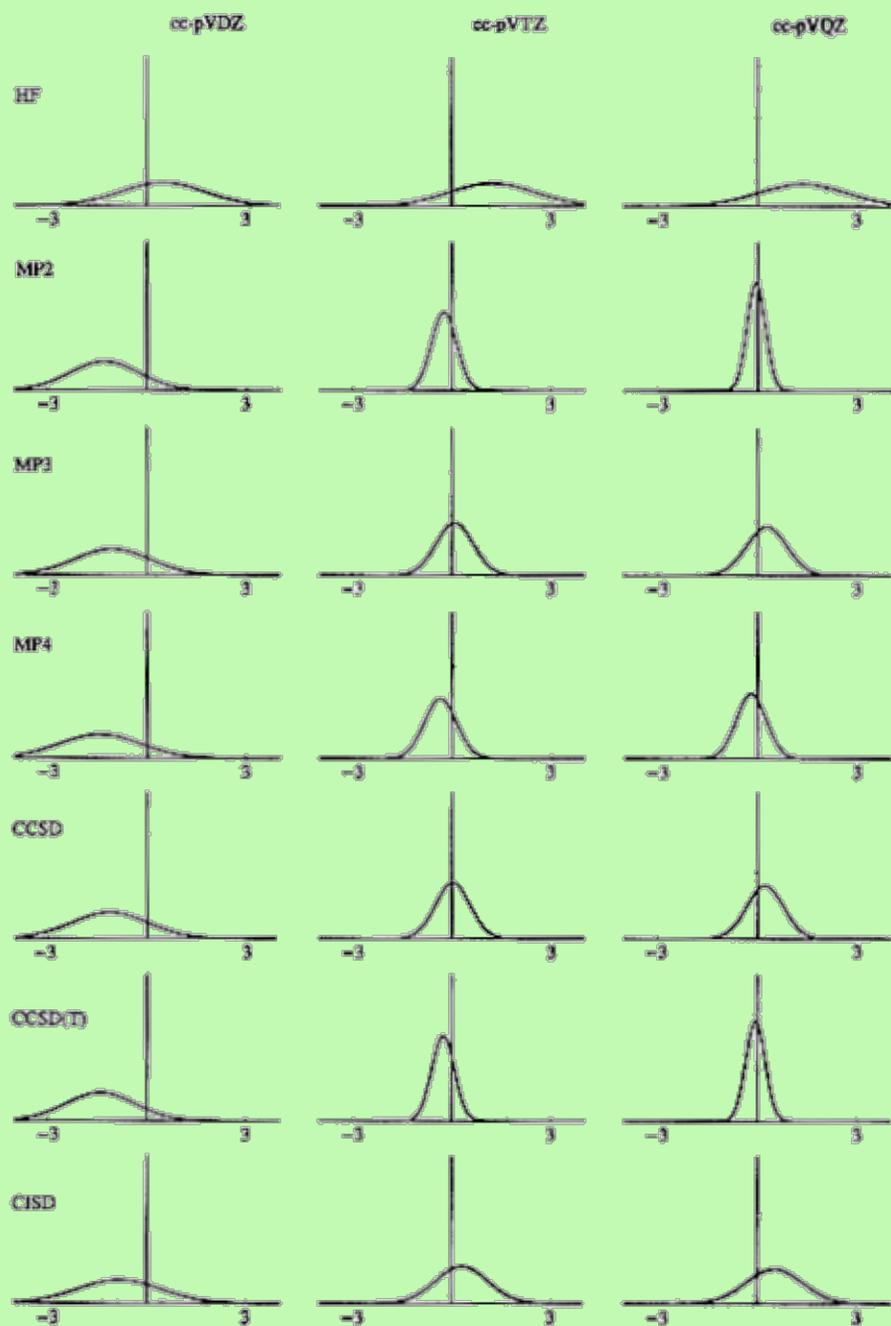
Remember that errors can be “crazy” too.



MPn energy errors (Hartrees) for the HF molecule at two bond lengths.

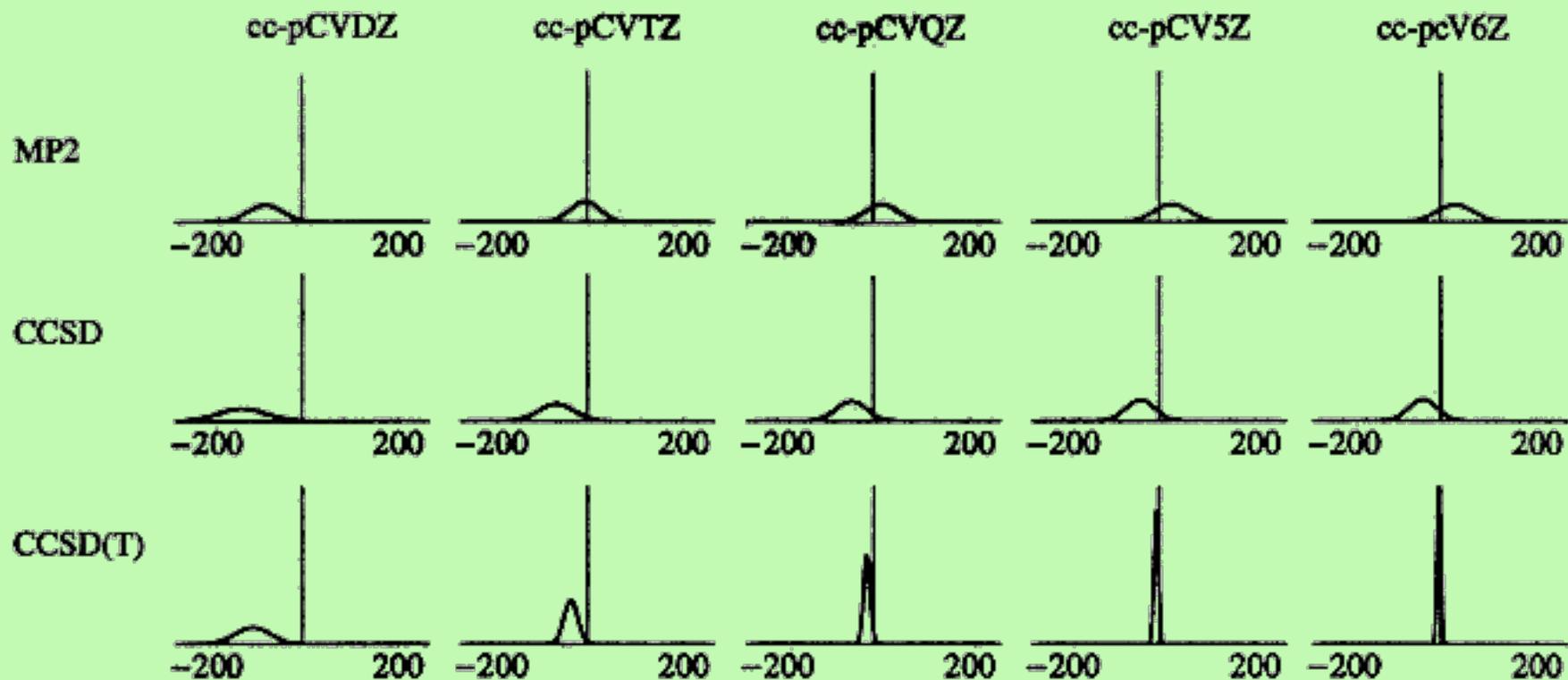


Error distribution (pm) in bond lengths with three basis sets and several methods compared to experimental bond lengths (line). Notice that systematic errors occur in some methods (e.g., HF) and that the range of errors varies with basis set size and with method for treating correlation.

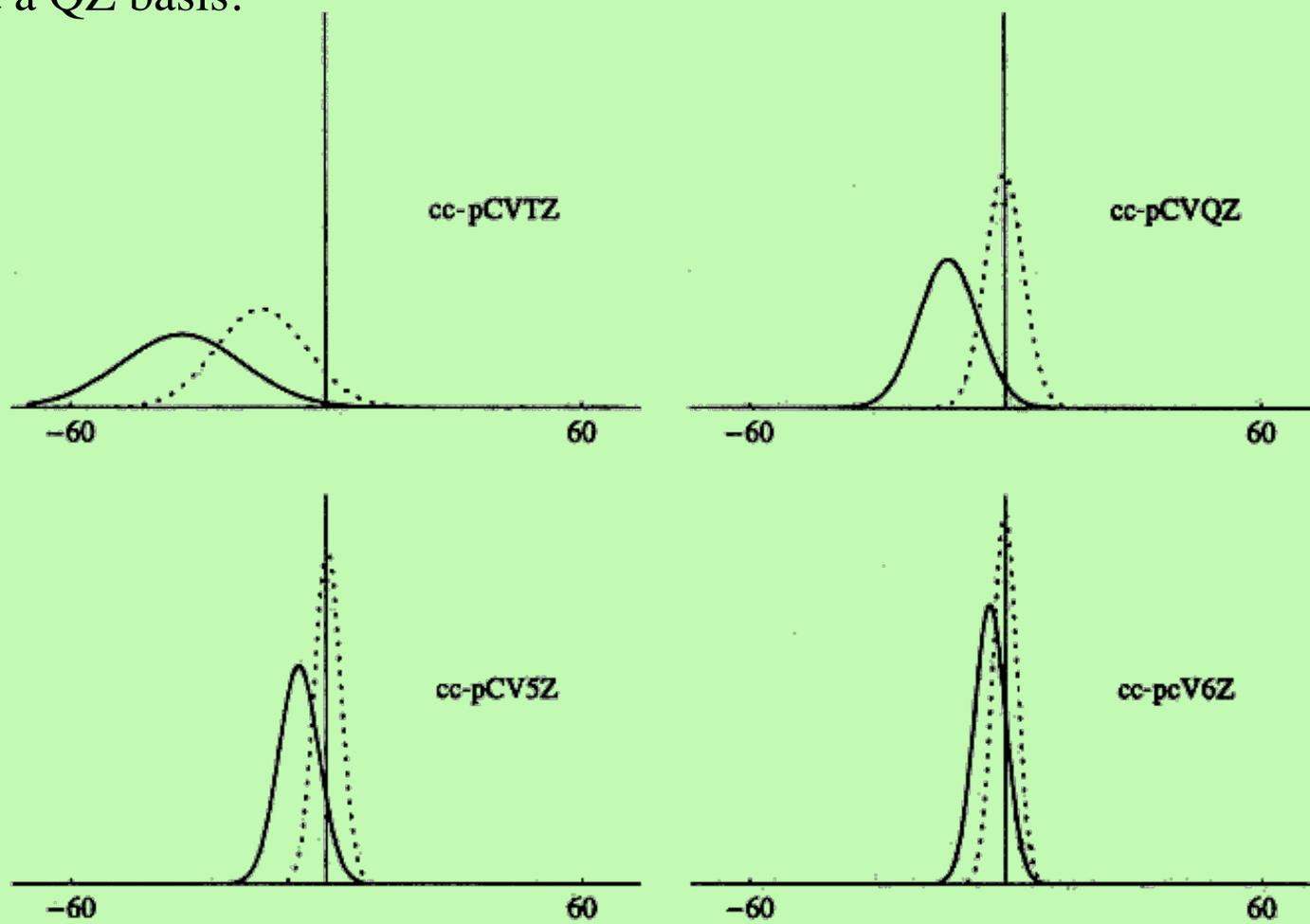


Error distribution in bond angles (deg) relative to experimental values for three basis sets.

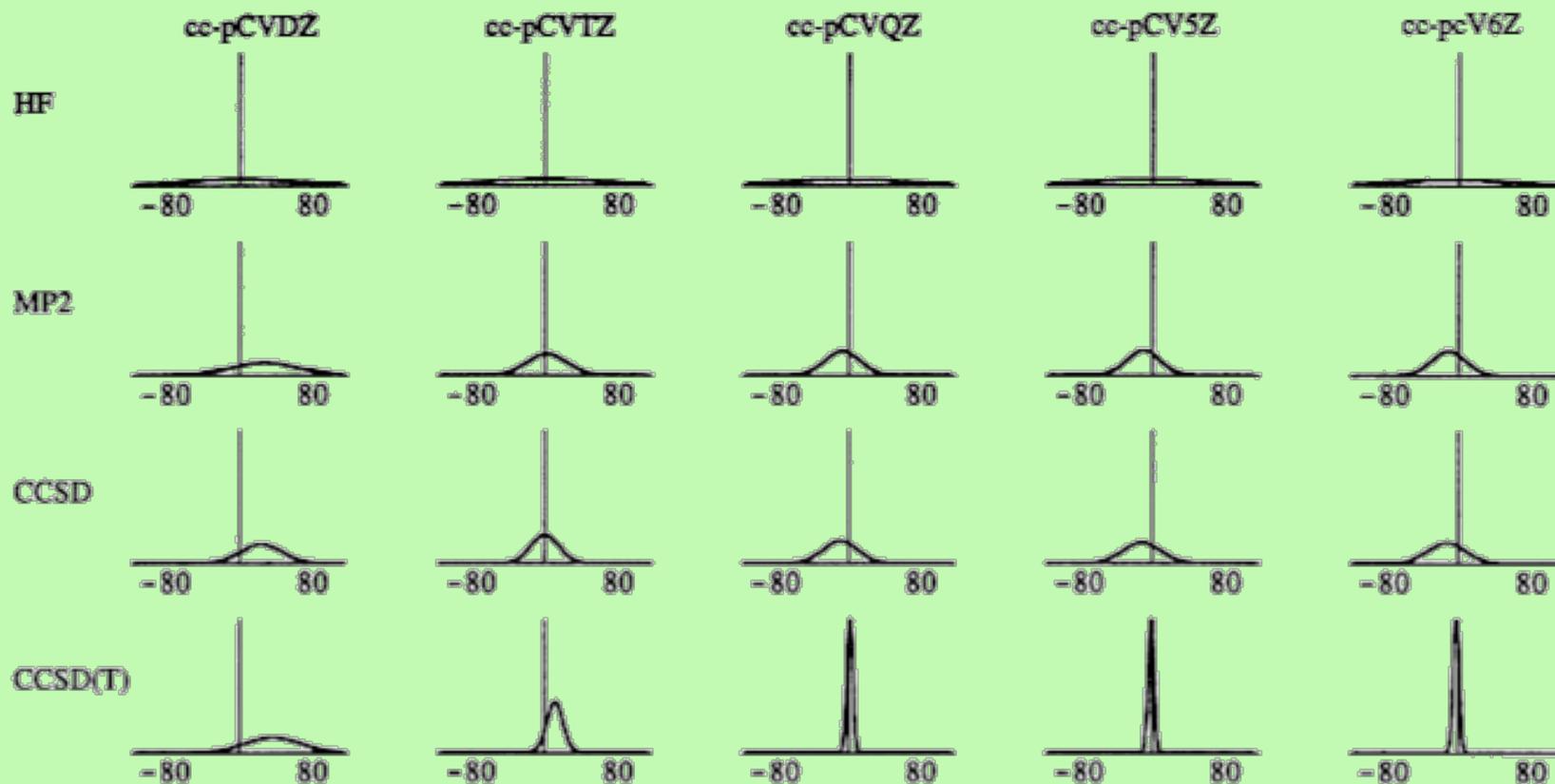
Error distribution in **atomization energies** (kJ/mol). Notice that it is very difficult (large basis and sophisticated treatment of correlation is needed) to achieve better than +/- 50 kJ/mol.



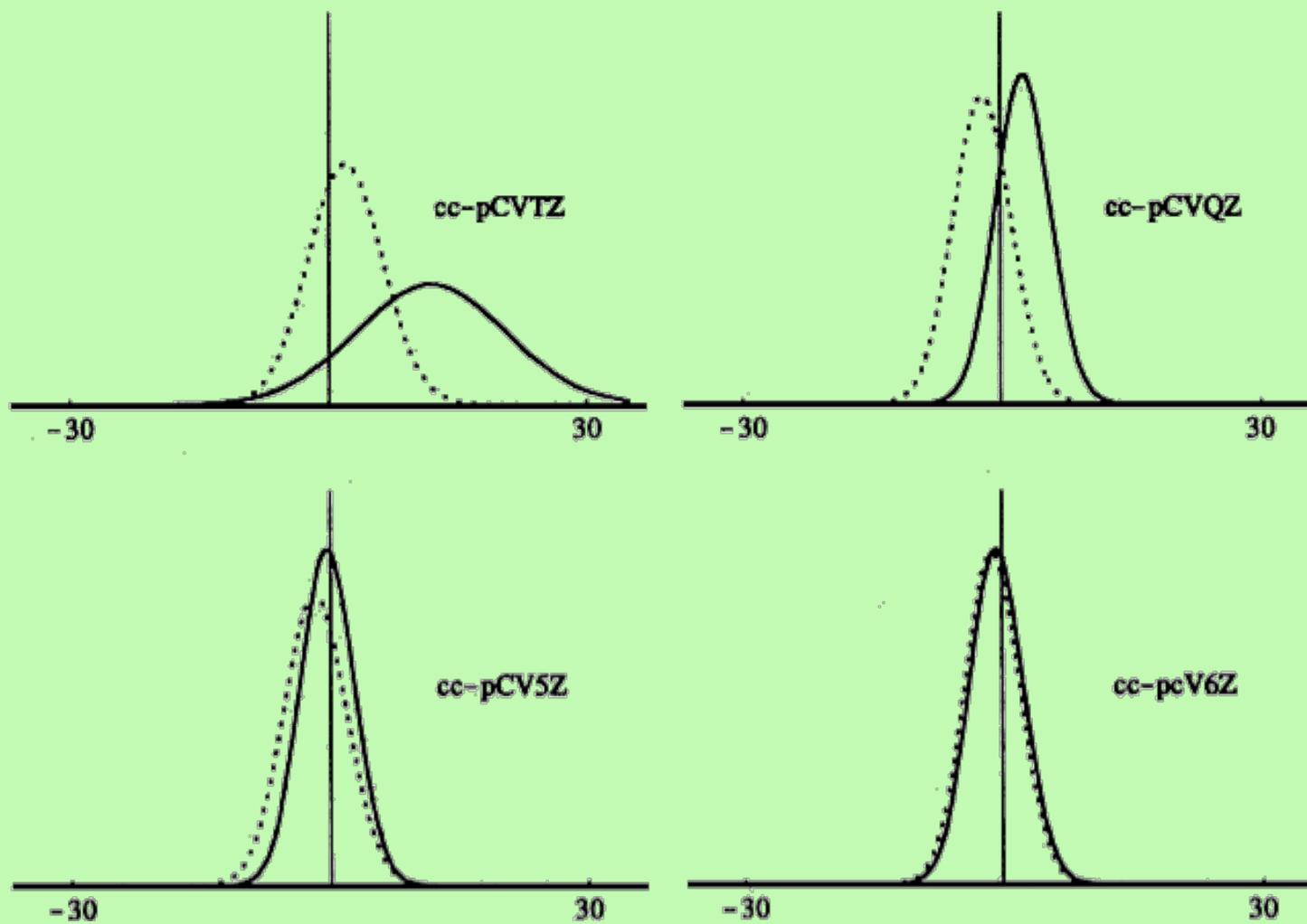
Error distribution in CCSD(T) computed atomization energies (kJ/mol) for four basis sets **with** (dotted) and **without** (full) CBS basis extrapolation. Notice that basis extrapolation helps, but it is good to use at least a QZ basis.



Error distribution in reaction enthalpies (kJ/mol) for five basis sets and various methods. Note that to get below  $\pm 40$  kJ/mol requires inclusion of correlation and a TZ or larger basis.



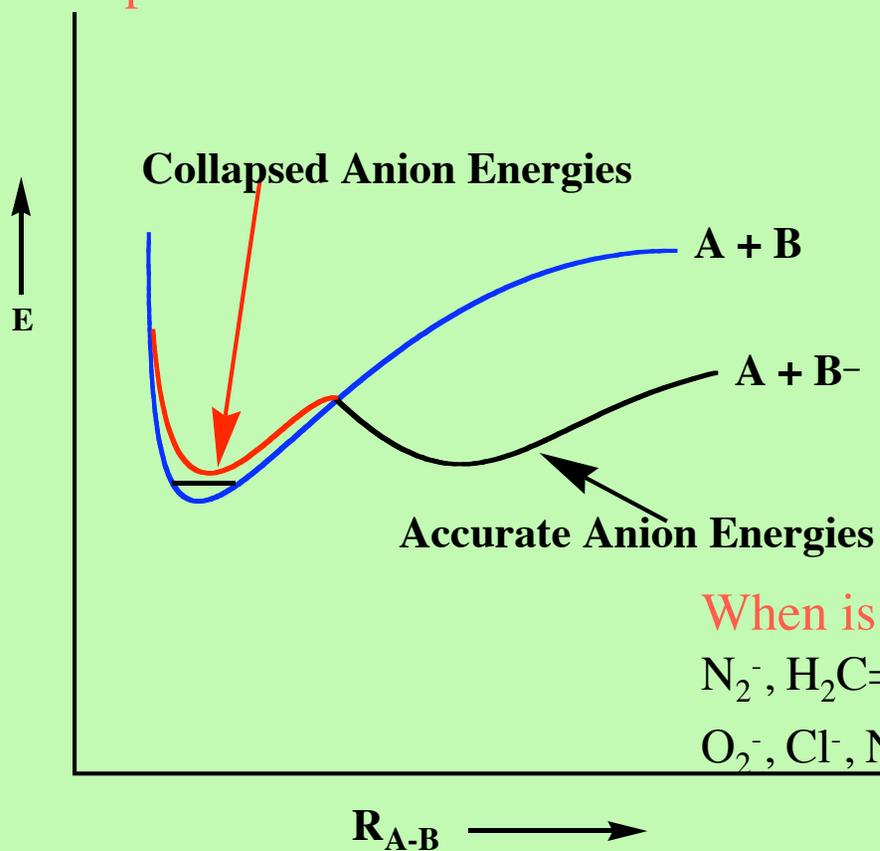
Error distribution in CCSD(T) computed reaction enthalpies (kJ/mol) with (dotted) and without (solid) CBS basis extrapolation. Notice that basis extrapolation helps for TZ and QZ bases.



Special *Tricks* are needed for calculating an anion's energy when it lies above the energy of the neutral.

Straightforward **variational** calculations will “collapse” to produce a wave function and energy appropriate to the neutral molecule plus a free electron with low energy.

**Example** of stable  $B^-$  and unstable  $AB^-$



When is this needed?

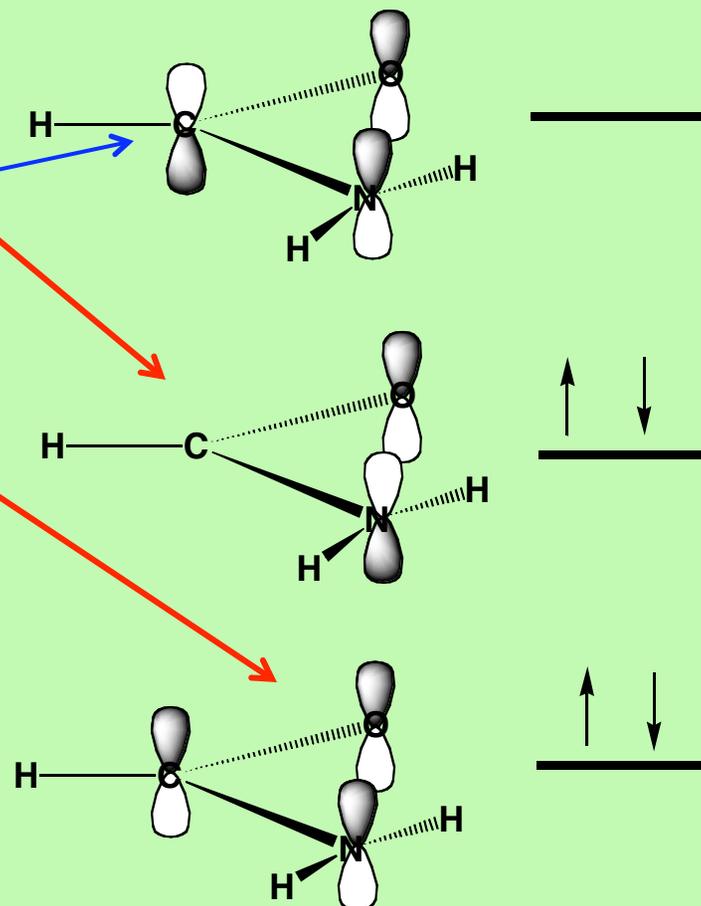
$N_2^-$ ,  $H_2C=CH_2^-$ ,  $SO_4^{2-}$  are all electronically unstable.

$O_2^-$ ,  $Cl^-$ ,  $NO_2^-$  are all stable.

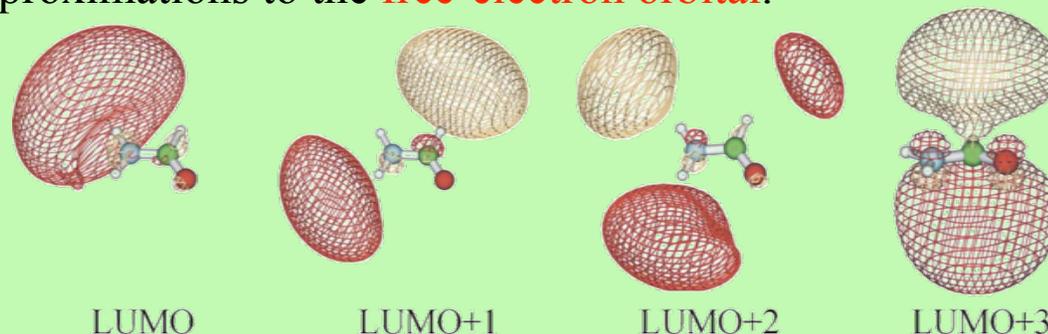
For **metastable anions** that can eject of an electron, **one cannot employ variation-based** tools because the lowest-energy state corresponds to that of a free electron (infinitely distant and with zero velocity) plus a system with one fewer electron. Standard methods suffer variational collapse and converge to such “free-electron” descriptions. Let’s consider formamide near its equilibrium geometry and its  $\pi$ -symmetry MOs.

The **lowest two  $\pi$  MOs** describe the delocalized  **$\pi$  bonding** and **non-bonding** orbitals. The unoccupied MO is the anti-bonding  $\pi^*$  orbital.

Even methods such as Møller-Plesset perturbation theory (**MP**) and coupled-cluster theory (**CC**) **suffer** from this problem **because they are based on a Hartree-Fock** (HF) self-consistent field (SCF) initial starting point that is intrinsically variation-based.

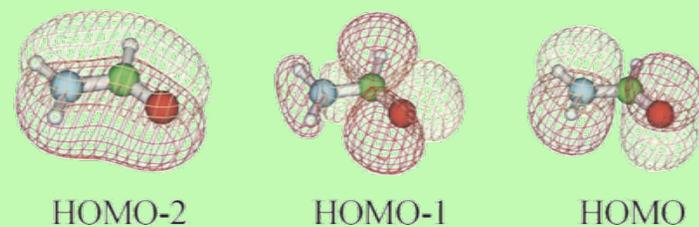


An SCF (aug-cc-pVDZ) calculation produces the orbitals shown below. The energies for HOMO-2 and HOMO are -15.4 and -11.5 eV, respectively. HOMO-1 is a lone pair orbital on the oxygen atom. The energy of LUMO is 0.72 eV, which suggests that an electron of 0.72 eV might attach to produce the formamide anion. However, the LUMO is not even of  $\pi^*$  symmetry, nor is the LUMO+1 or the LUMO+2. In fact, these three unoccupied orbitals do not have any significant valence character; most of their amplitude is outside the formamide molecule's molecular skeleton. They are, within the finite atomic orbital basis used, approximations to the free-electron orbital.

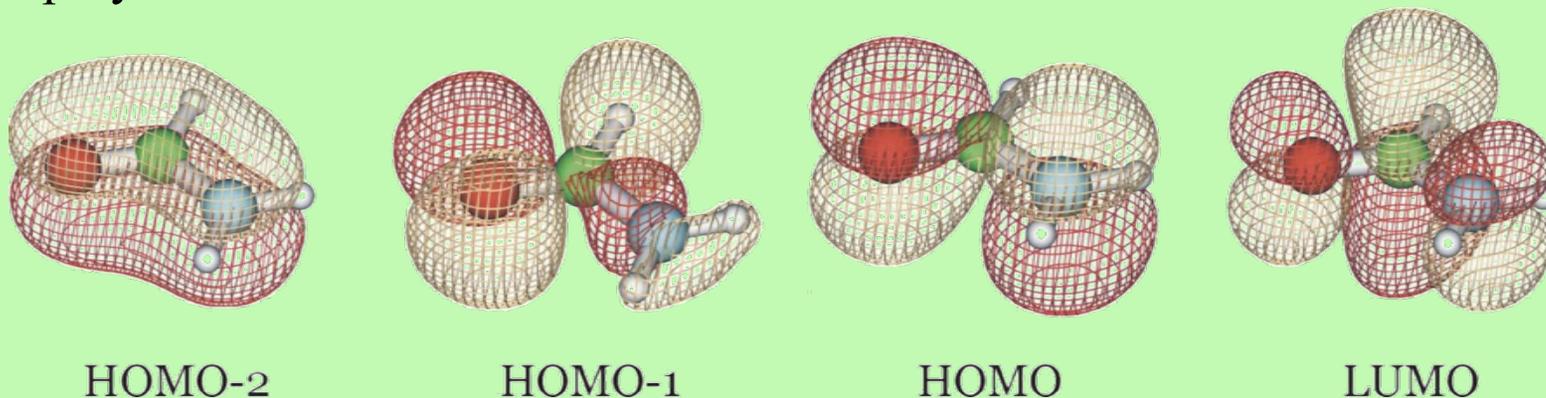


The lowest unoccupied orbital of  $\pi^*$  character is LUMO+3, which has an energy of +2.6 eV.

However, in a different atomic orbital basis, the lowest unoccupied orbital of  $\pi^*$  symmetry would not necessarily be LUMO+3, nor would it necessarily have an orbital energy near 2.6 eV.



For an idea of how these orbitals look for other atomic orbital basis sets, we show below four of the orbitals obtained when a 6-31G\*\* basis is employed.



HOMO-2 and HOMO are still  $\pi$  bonding and non-bonding and HOMO-1 is still an oxygen lone pair orbital, but now LUMO is the  $\pi^*$  anti-bonding orbital.

It is important to notice that the desired  $\pi^*$  orbital may be the LUMO in one basis but might be another orbital in a different basis as it is in the examples shown above. It is the virtual orbitals that vary a lot from basis to basis because some try to approximate continuum orbitals.

So, the **energy of the LUMO can not be trusted** to give the EA because most of the low-energy vacant orbitals are attempts, within the finite orbital basis used, to represent a free electron plus a neutral formamide molecule. This illustrates the **variational collapse** problem mentioned above.

Consider an electron approaching a formamide molecule from afar and decompose the wave function describing this “attached” electron into products of radial and angular terms:

$$\psi(r,\theta,\phi) = \sum_{L,M} \psi_{L,M}(r) Y_{L,M}(\theta,\phi).$$

Substituting such an expansion into the Schrödinger equation

$$\{-\hbar^2/2m r^{-2} \partial/\partial r(r^2 \partial/\partial r) + \hbar^2 L^2/2mr^2 + V\} \psi = E \psi$$

multiplying on the left by  $Y_{L,M}^*$  and integrating over  $\theta$  and  $\phi$ , gives

$$\{-\hbar^2/2m r^{-2} \partial/\partial r(r^2 \partial/\partial r) + \hbar^2 \langle L^2 \rangle / 2mr^2 + \langle V \rangle\} \psi_{L,M} = E \psi_{L,M}$$

where  $\langle V \rangle$  denotes the angular average of the electron-molecule potential

$$\langle V \rangle = \int Y_{L,M}^* V Y_{L,M} \sin\theta d\theta d\phi.$$

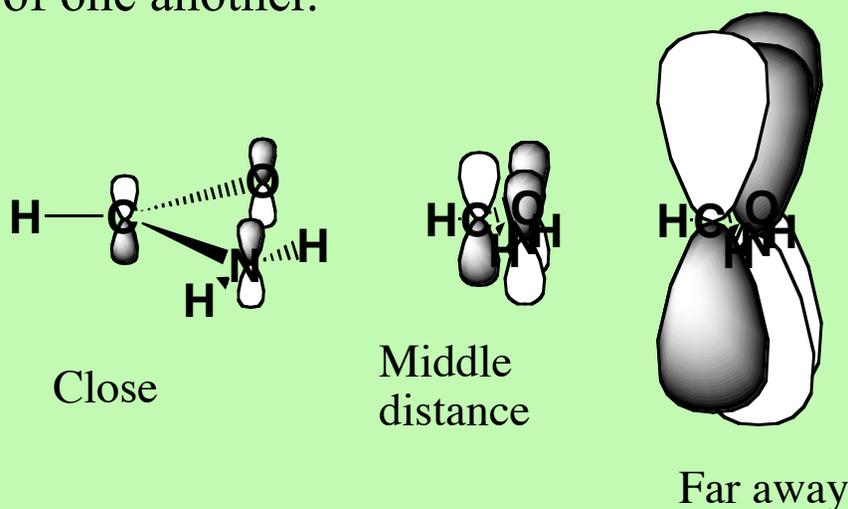
When the distance  $r$  of the electron from the molecule is large,  $\langle V \rangle$  is dominated by an attractive Coulomb factor if the electron is interacting with a cation, by a charge-dipole potential if the electron is interacting with a polar neutral molecule, and by a repulsive Coulomb factor if the electron is interacting with a negative ion.

The centrifugal potential

$$\hbar^2 \langle L^2 \rangle / 2mr^2$$

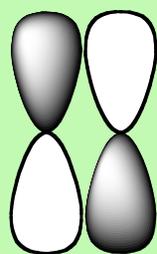
always varies as  $r^{-2}$

For formamide, the nodal character of the  $\pi^*$  orbital into which the incoming electron is to attach has dominant  $L = 3$  character. To see this, we view this orbital from a long distance at which its three nuclear centers are nearly on top of one another.

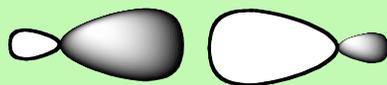


When viewed as having the O, C, and N nuclei on top of one another, this  $\pi^*$  orbital clearly has nodal properties like that of an f-orbital which is why  $L = 3$  is dominant at large- $r$ .

Some **L-values** (p, d, f, g, h, are  $L = 1, 2, 3, 5, 5$ ) of various anion orbitals



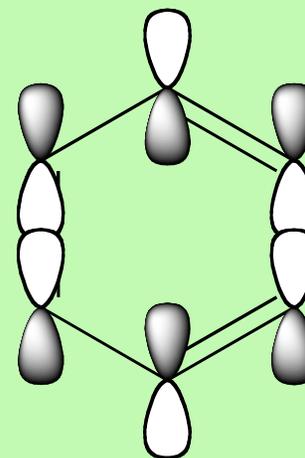
$\text{O}_2^- \ ^2\Pi$   
d wave



$(\text{RS})_2^- \ ^2\Sigma$   
p wave

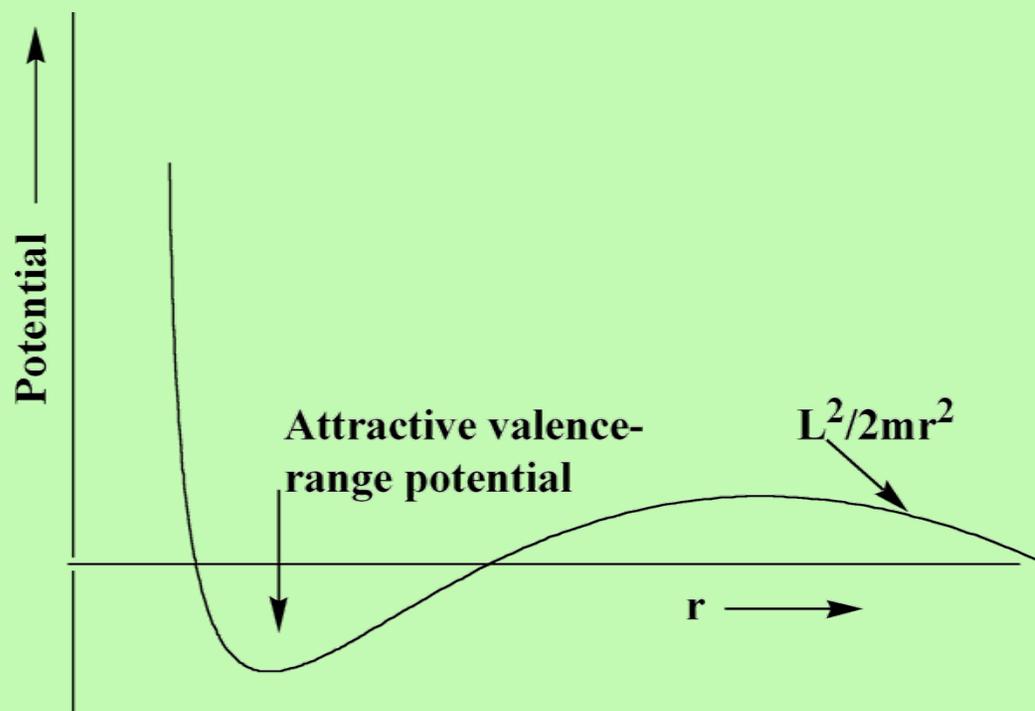


$\text{Mg}^- \ ^2P$   
p wave



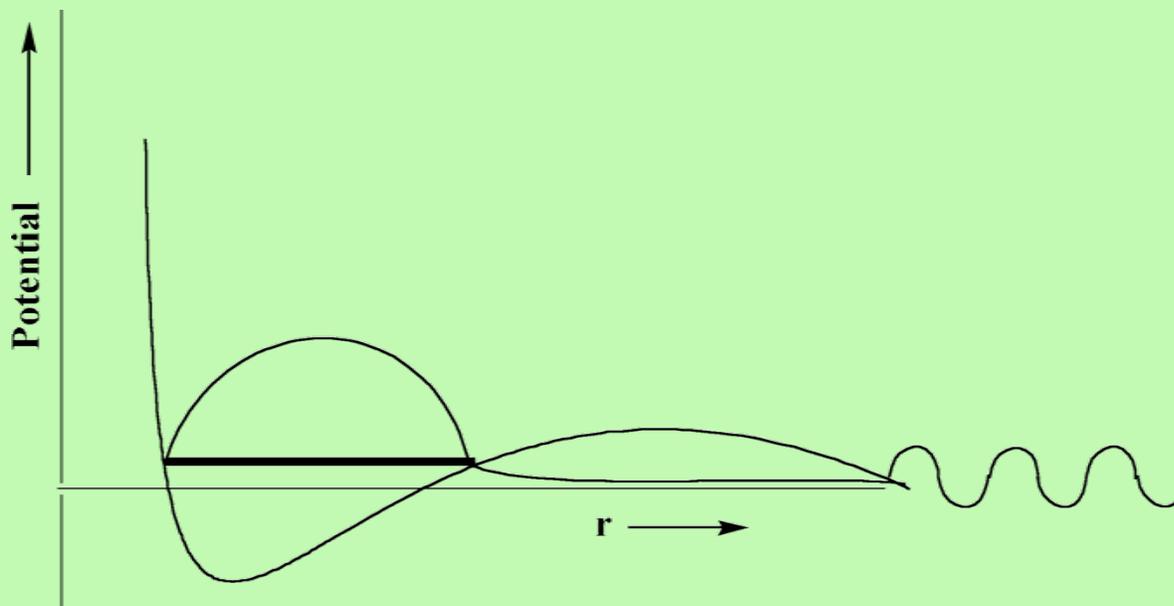
$\text{C}_6\text{H}_6^-$   
h wave

An electron in an orbital having angular momentum  $L$  experiences an effective radial potential (i.e., the sum of  $\langle V \rangle$  and the centrifugal potential) that varies as shown below for a neutral molecule.

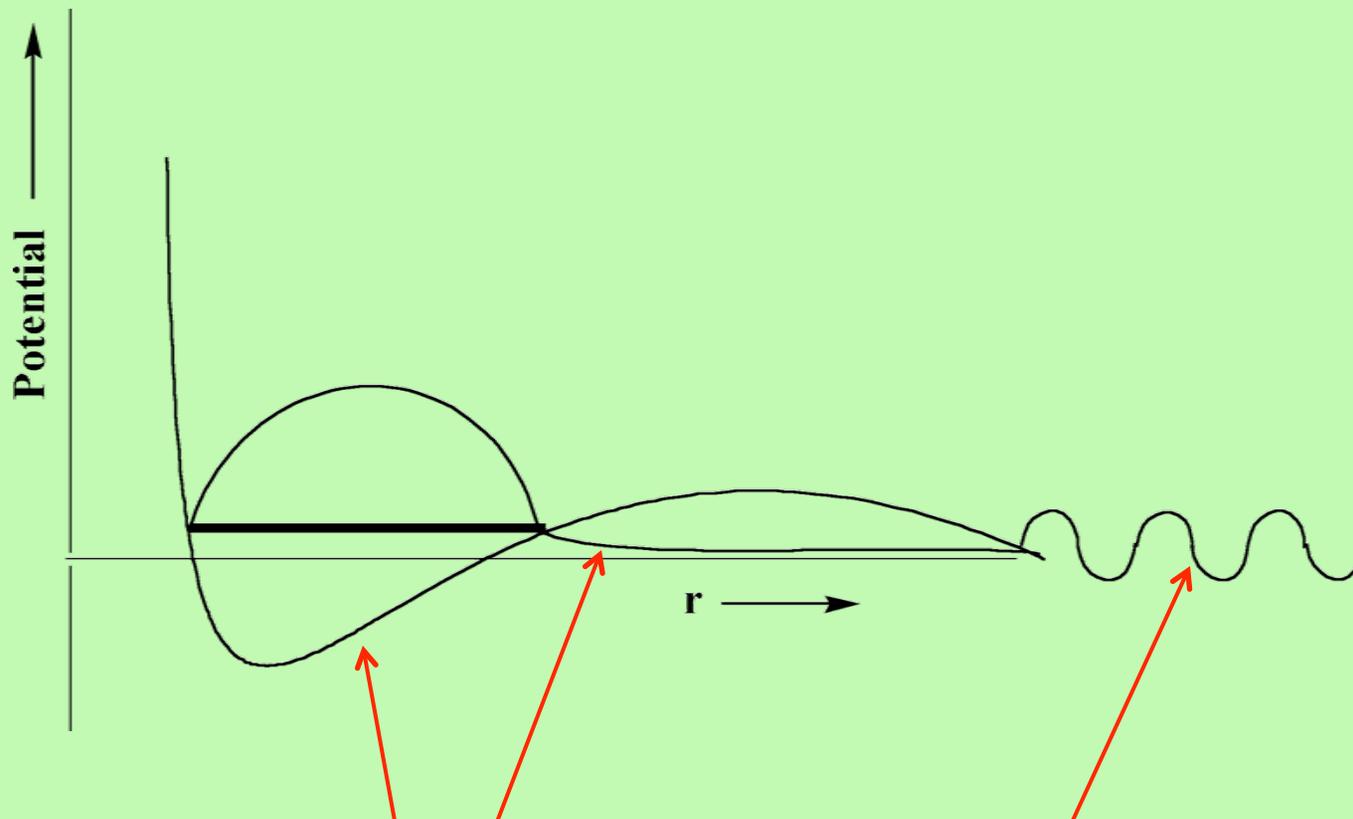


For an electron interacting with an anion to form a dianion, the repulsive long-range part of the potential also includes a Coulomb term  $e^2/r$ . In such cases, the barrier that acts to constrain the electron in the metastable state arises from both Coulomb and centrifugal factors.

For **formamide**, the component of the potential generated by the attractive valence-range influences of the O, C, and N centers is not strong, so **no bound state** of the anion will exist. For such a case, only the metastable  $L = 3$  **shape resonance** state will occur and it will have an energy (the heavy horizontal line) and a radial wave function as shown below.

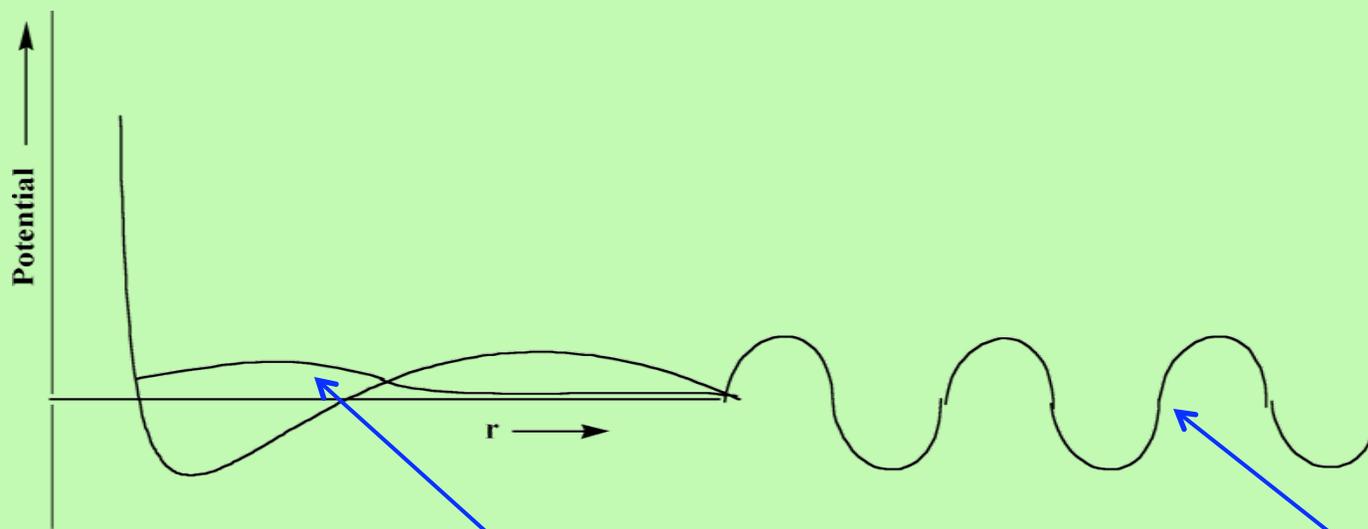


For another example, the  ${}^2\Pi$  state of NO is electronically stable relative to  $\text{NO}^+$ , but the  ${}^2\Pi$  state of the isoelectronic species  $\text{N}_2^-$  is metastable. The increased electronegativity of the oxygen atom in NO compared to that of the nitrogen atom in  $\text{N}_2^-$  is enough to make the valence-range potential attractive enough to make NO stable.



In the **valence region**, the resonance function has large amplitude, suggesting that the electron is rather localized, it decays exponentially in the classically forbidden tunneling region, and it has sinusoidal oscillations beyond this region with the local de Broglie wavelength relating to the electron's kinetic energy.

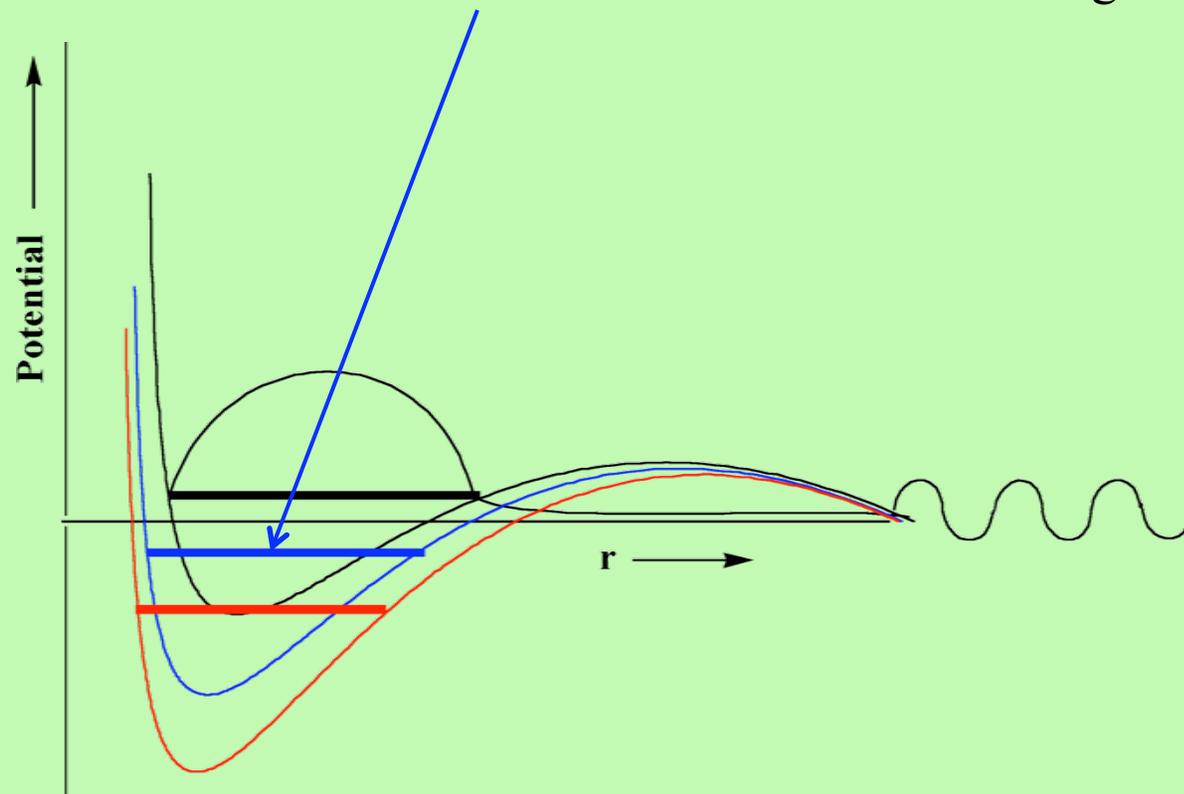
However, at energies both above and below that of the shape resonance state, there exists a continuum of other states. Those lying below the resonance energy vary with  $r$  as shown below.



Little amplitude in the valence region; large amplitude at large- $r$ .  
Longer de Broglie wavelength and thus lower energy than the resonance state.

There are also non-resonant states lying energetically above the shape resonance-little amplitude in the valence region, larger amplitude at large- $r$ , with shorter de Broglie wavelength corresponding to higher kinetic energy.

So, how can we identify and characterize the resonance wave function (and its energy) when it is “buried” within a continuum of higher- and lower-energy states? In the nuclear charge stabilization method, we attempt to smoothly slightly enhance the valence-region attractive character of the potential  $V$  that the attached electron experiences to an extent that pulls the energy of the metastable resonance state below zero thus rendering it stable.



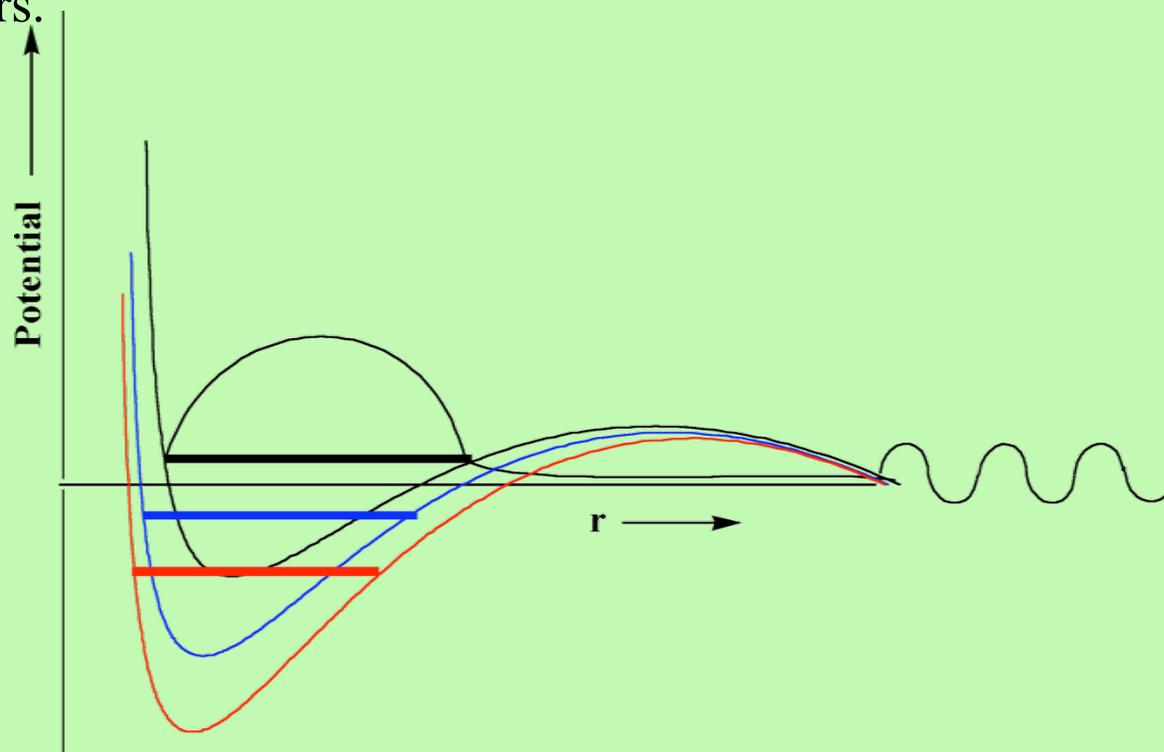
We do this by adding to the  $V_{e,n}$  potential

$$V_{e,n} = \sum_{j=1,N} \sum_{K=1,M} (-Z_K/|\mathbf{r}_j - \mathbf{R}_K|)$$

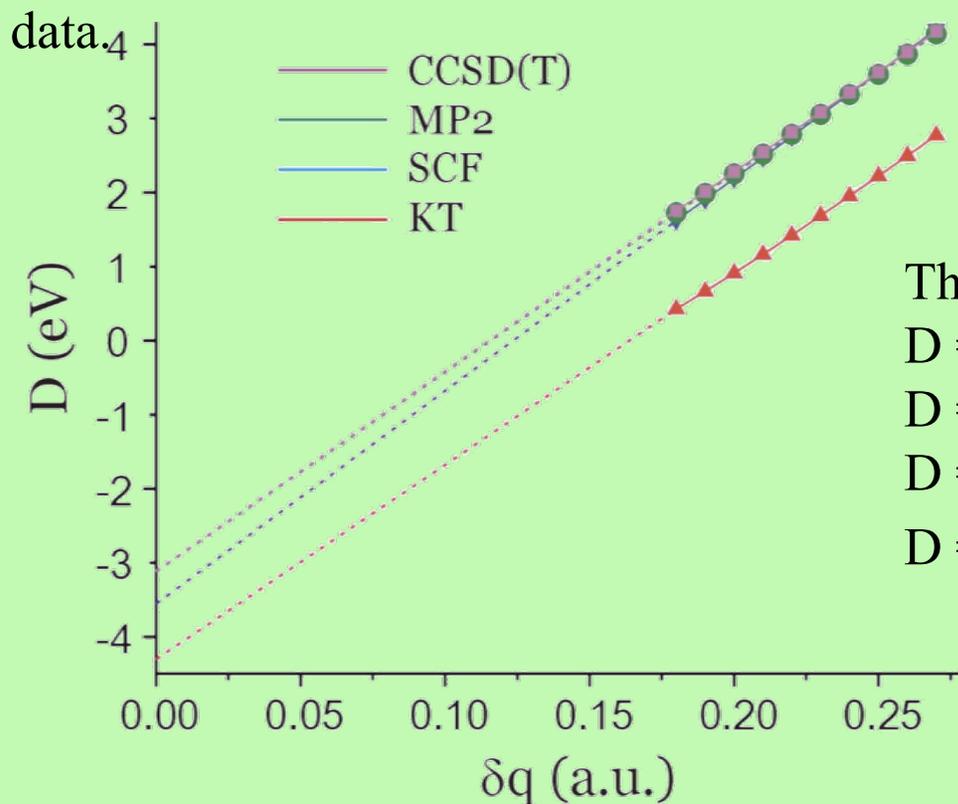
An amount (for example, for the O, C, and N nuclei of formaldehyde)

$$\delta V_{e,n} = -\delta q \sum_{j=1,N} [ (1/|\mathbf{r}_j - \mathbf{R}_O|) + (1/|\mathbf{r}_j - \mathbf{R}_C|) + (1/|\mathbf{r}_j - \mathbf{R}_N|) ]$$

that acts to differentially stabilize the electron's potential energy near these nuclear centers.



The key thing to notice that is, **if the nuclear charge enhancement is large enough**, the valence-range component of the potential will be lowered enough to render **the resonance state bound rather than metastable** and thus **amenable to studying using conventional variational-based** quantum chemistry tools. In this manner, one can carry out conventional calculations on the nuclear charge enhanced species for a series of  $\delta q$  values (all of which must be large enough to render the desired state bound) and then extrapolate to  $\delta q \rightarrow 0$  to allow the resonance state to be identified from the finite- $\delta q$  calculations'

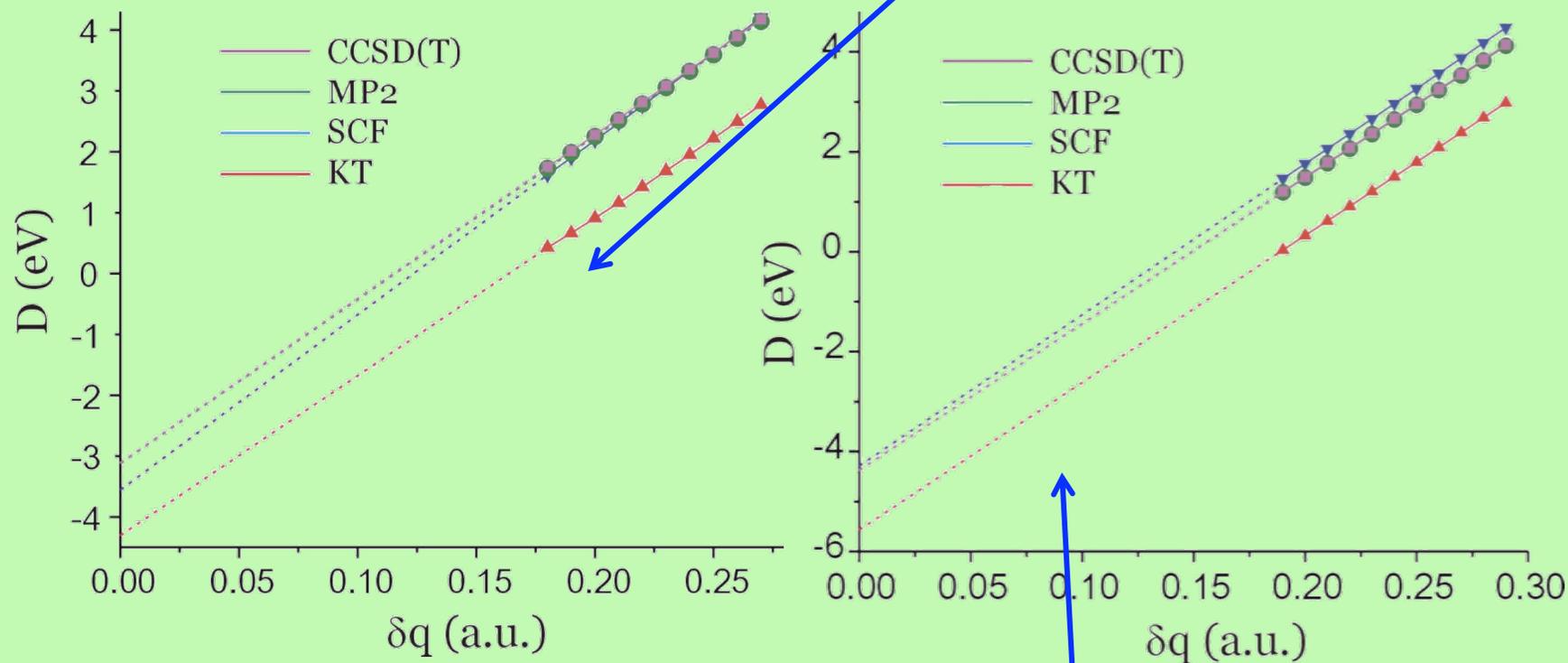


The  $\delta q \rightarrow 0$  extrapolated energies:  
D = -4.3 eV (KT, red)  
D = -3.6 eV (SCF, blue)  
D = -3.1 eV (MP2, green),  
D = -3.1 eV (CCSD(T), magenta)

In practice, to use the nuclear charge stabilization method, one (for a series of  $\delta q$  values)

1. Identifies those nuclei over which the valence component of the desired resonance state's orbital will be distributed.
2. Modifies the nuclear charges of these nuclei (one need not use equal charge increments for all the nuclei) by increasing them by an amount  $\delta q$ ;
3. Carries out a standard, bound-state, quantum calculation (SCF, MPn, coupled-cluster, or whatever) on the electron-attached and non-attached states using the scaled nuclear charges to obtain attached ( $E^*$ ) and non-attached ( $E$ ) state energies, after which
4. One plots the energy difference ( $E-E^*$ ) vs.  $\delta q$  but using only  $\delta q$  values large enough to render  $E-E^* > 0$  (i.e., to make the attached state bound relative to the non-attached state), and
5. One then extrapolates the plot to  $\delta q \rightarrow 0$  to obtain an estimate of the energy of the electron-attached state relative to that of the parent non-attached species (i.e., in the extrapolation, one will find  $E-E^*$  negative, meaning the electron attached species lies above its parent).

In the figure show earlier, we show Koopmans' theorem, SCF-level, MP2-level, and coupled-cluster level energy differences (D) for the formamide and formamide  $\pi^*$  anion obtained using the aug-cc-pVDZ basis set discussed earlier.

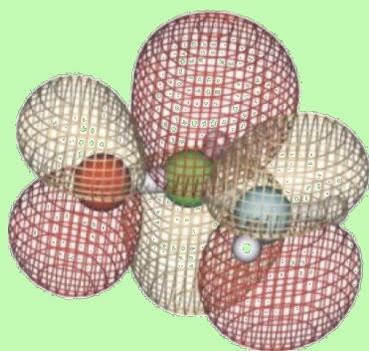


When analogous nuclear charge stabilization calculations are performed using the 6-31G\*\* basis, the plot shown here results.

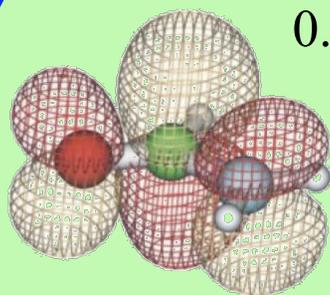
These extrapolations represent the nuclear charge stabilization's predictions for the energy of the anion's metastable  $\pi^*$  resonance state relative to that of the neutral for each level of theory.

In addition, below we show the  $\pi^*$  LUMO obtained for the aug-cc-pVDZ basis set for  $\delta q = 0.19$  and  $0.26$  to show how it differs significantly from the LUMO obtained in the non-scaled calculation which, as we explained earlier, cannot be trusted to relate to the desired resonance state. Clearly, this orbital has the desired valence character and nodal pattern. For  $\delta q = 0.26$  it is more compact than for  $\delta q = 0.19$  because of the enhanced nuclear attraction in the former case.

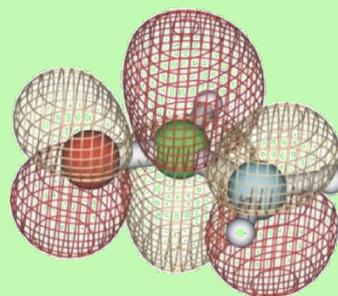
For the 6-31G\*\* basis, this same orbital is shown below also for  $\delta q = 0.19$  and  $\delta q = 0.26$ .



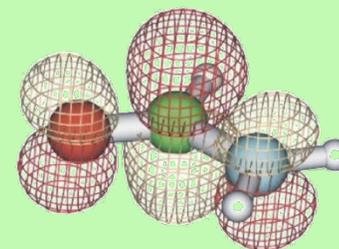
$\delta q=0.19$



$\delta q=0.26$



$\delta q=0.19$



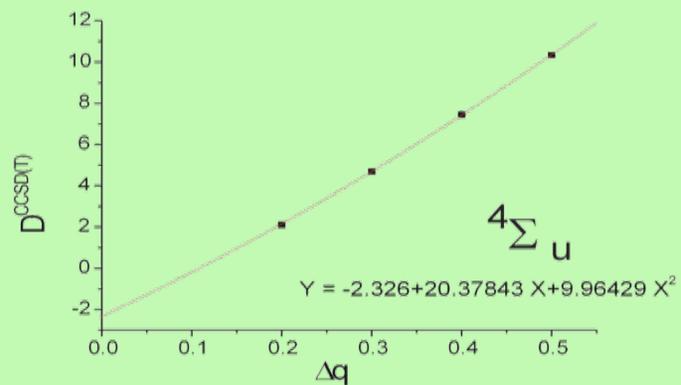
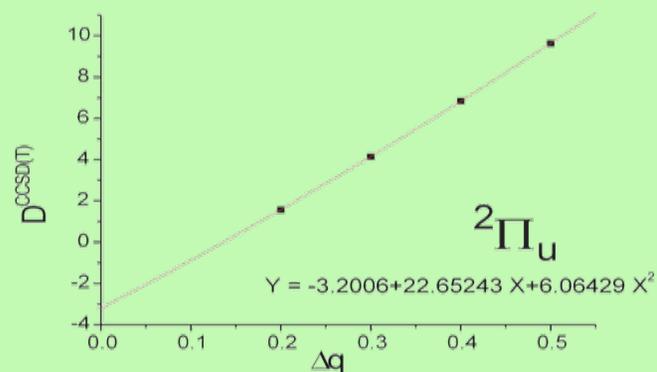
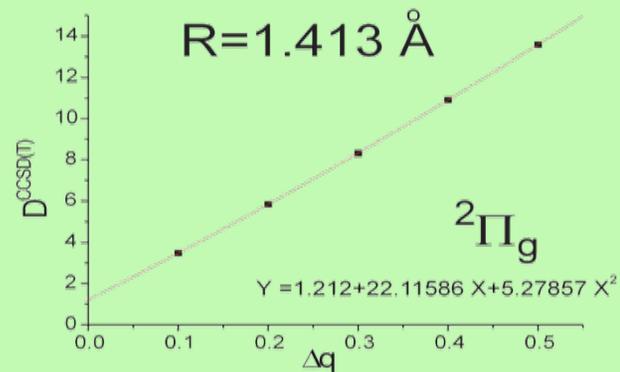
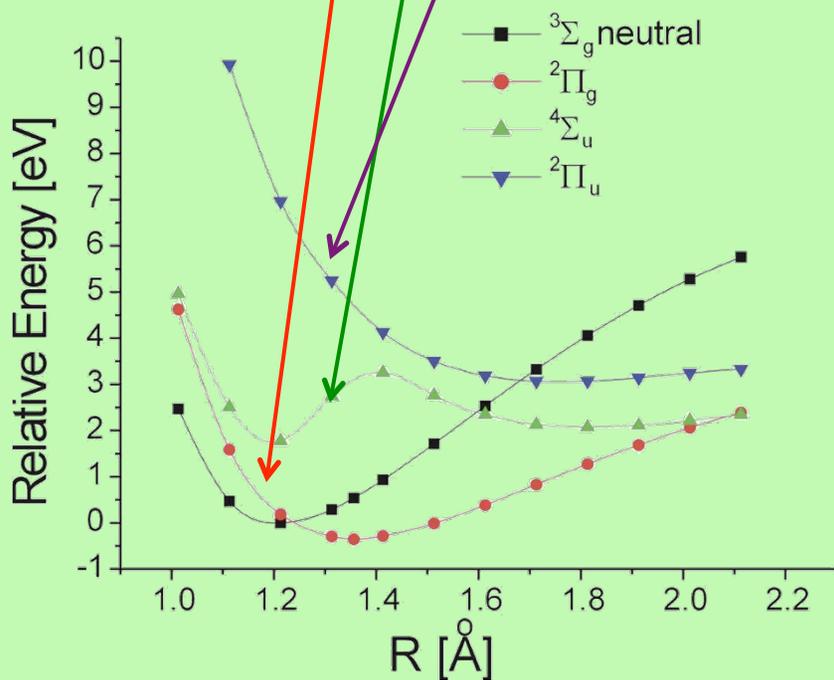
$\delta q=0.26$

We see that the qualitative character of the desired  $\pi^*$  orbital does not depend on the basis set employed although the quantitative values of the resonance state energy do.

For the larger basis and using the highest-level of theory (the CCSD(T) data), the  $\pi^*$  attached anion is predicted to lie 3.1 eV above the neutral formamide at the neutral's equilibrium geometry.

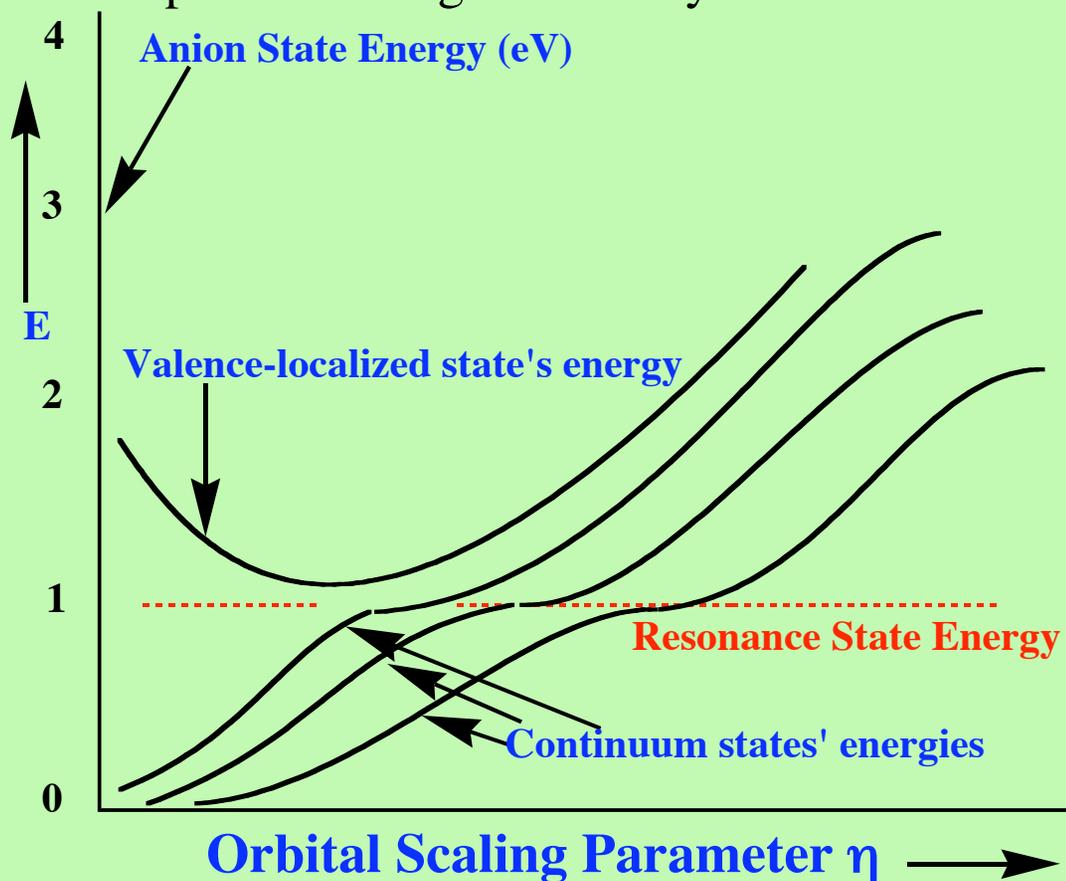
Experiments using so-called electron transmission spectroscopy methods find a resonance state to lie ca. 2 eV above the neutral, so one can see that obtaining accurate estimates of the energies of such metastable states is difficult even when rather good atomic basis sets are employed.

Consider calculating the Born-Oppenheimer energies of various states of  $O_2^-$ . All three lowest states have bond lengths where the anion is electronically unstable.

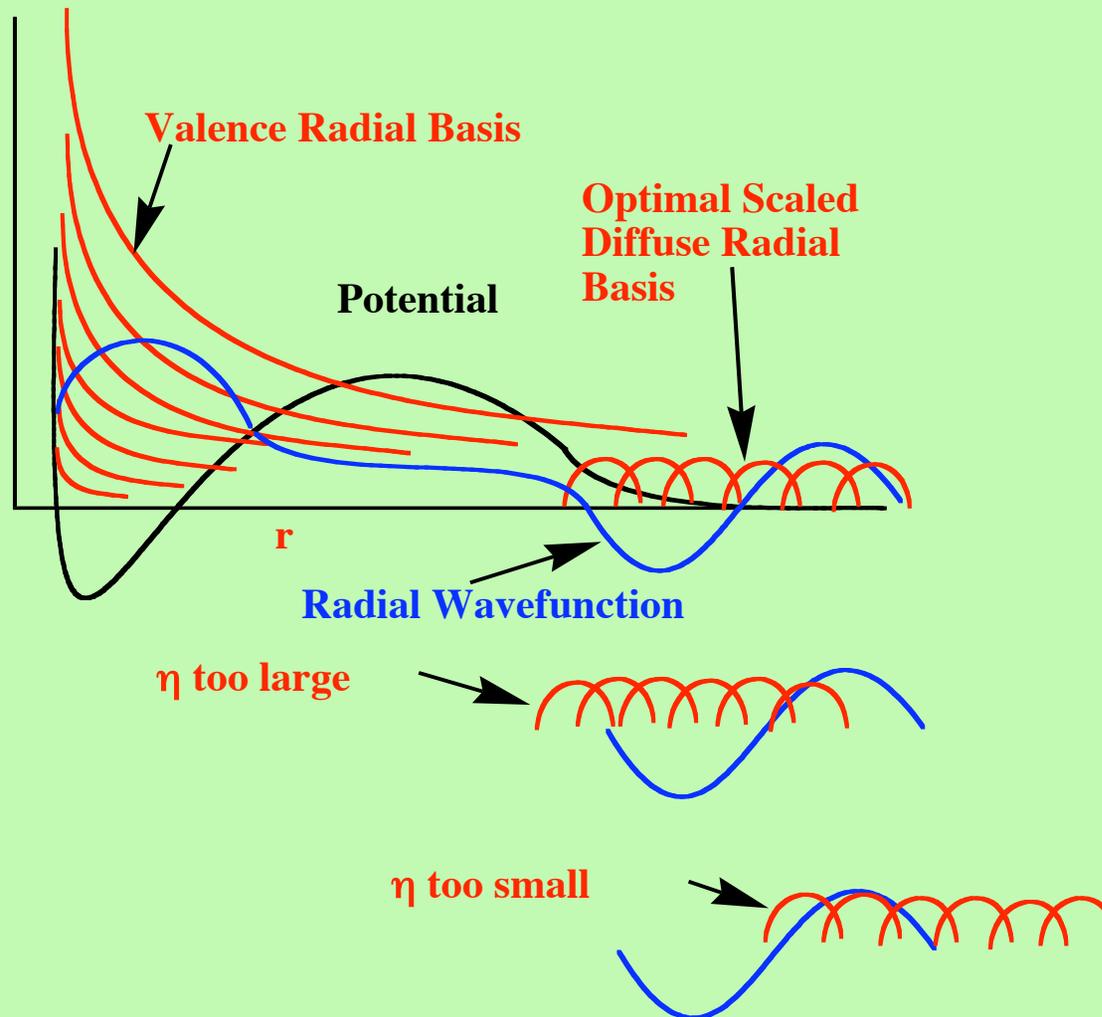


In the *stabilization method* one computes the anion-neutral energy difference in a series of basis sets whose more diffuse basis functions' exponents  $\alpha$  are scaled  $\alpha \rightarrow \eta \alpha$ . Plotting the anion-neutral energy differences vs  $\eta$  produces a stabilization plot that can be used to determine the metastable state's energy.

These energies grow with  $\eta$  because  $T$  scales as  $\eta^2$ . This method requires one to compute the energies of many anion states.



At certain  $\eta$  values, the diffuse basis functions can be combined to describe the de Broglie  $\lambda$  of the asymptotic  $\psi$  and can match  $\psi$  and  $d\psi/dr$  throughout.



The lower-energy curves describe the dominantly-continuum solutions' variation with  $\eta$ . When one of these solutions gains the proper de Broglie and can match the energy of the valence-localized state, an avoided crossing occurs. The energy of this crossing is the resonance energy.

